

2. Production and Use of Paint Products

2.1 Production

(a) Production processes

The modern manufacture of paints, which are generally made in batches, involves three major steps: (i) mixing and grinding of raw materials; (ii) tinting (shading) and thinning; and (iii) filling operations (US Environmental Protection Agency, 1979), as illustrated in Figure 1.

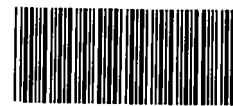
To produce a batch of paints, manufacturers first load an appropriate amount of pigment, resin and various liquid chemicals into a roller mill, which is a large, hollow, rotating steel cylinder. Mills for grinding primer or dark pigments are partly filled with steel balls that measure about 1–2 cm in diameter. Mills for grinding light colours usually contain flattened ceramic spheres (pebbles) that measure about 3–4 cm in diameter. Depending on the type of mill used, the grinding process lasts about 24 h or until the pigment has been ground to a sufficiently fine paste. After the pigment has been ground, more resin and solvent are added to the paste in the mill and the paste is 'let down', that is, pumped out of the mill through a strainer which removes the grinding media to a holding tank.

Until the 1930s, drying vegetable oils, primarily linseed oil, were used as binders in paints and as liquids for grinding. Since these oils were relatively poor pigment wetters, considerable energy was required for the grinding (dispersion) steps. Earlier dispersion techniques which involved pebble, steel ball or roller mills were replaced during the 1960s by high-speed equipment which was first used to dissolve large chips of pigment dispersed in solid binders. As pigment production and wetting characteristics improved, pigments were dispersed satisfactorily in high-speed dissolvers (Schurr, 1981).

The 'tinting' step involves comparing samples in the holding tank with colour standards. Small amounts of shading pastes, which are highly concentrated blends of ground pigments, and a vehicle are added as required to match the standard. After the batch has been shaded to specifications, it is thinned to the desired viscosity by the addition of solvent, filtered and poured into containers for shipment (Schurr, 1981).

The complexity of paint technology is indicated by the numerous types and number of raw materials required. A plant that produces a broad line of trade, maintenance and industrial paints requires over 500 different raw materials and purchased intermediates, including oils, pigments, extenders, resins, solvents, plasticizers, surfactants, metallic driers and other materials (Federation of Societies for Paint Technology, 1973).

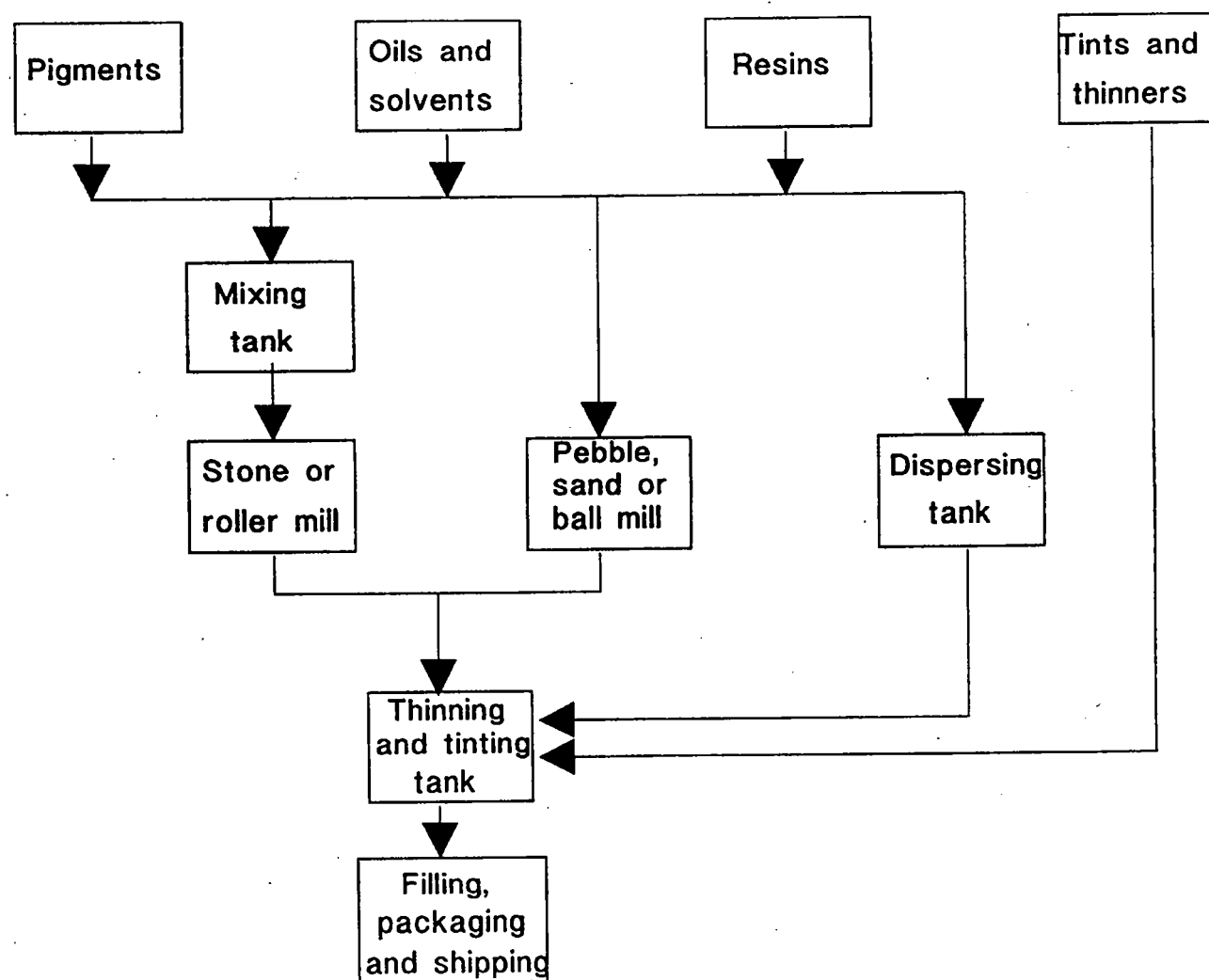
The modern manufacture of unpigmented lacquers is generally a cold-cutting or simple mixing operation. For example, cellulose nitrate solutions are made by adding the nitrated cellulose from alcohol-wet cotton to the solvent mixture and agitating for 1–2 h in a paddle or turbine blade mixer. Alkyd resins, which are supplied in solution, can be added directly to the cotton-based solution. Hard resins may be dissolved separately, usually in toluene, and added as solutions, or the lumps may be dissolved directly in the cotton-based



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Fig. 1. Process for manufacturing solvent-based paints^a



^aFrom US Environmental Protection Agency (1979)

solution by stirring. Liquid plasticizers are then simply poured or pumped into the mixing tank (Hamilton & Early, 1972).

In pigmented lacquer manufacture, the pigments are first dispersed in ball mills with plasticizers, such as dibutyl phthalate, after which natural or synthetic resins are added. Cellulose nitrate (or cellulose acetate) is then added and all the components are mixed in a vertical mixer or churn before the finished product is run off into containers (Browne, 1983).

Modern manufacture of varnish is carried out in jacketed and enclosed kettles or set pots, and the required high temperature is achieved by different methods, including the use of heat-transfer media (Browne, 1983).

(b) Production figures

Traditionally, two distinct types of coatings are produced – trade sale paints and industrial product finishes (Kline & Co., 1975).

Trade sale paints are sold through a variety of distribution channels to builders, contractors, industrial and commercial users and government units, as well as to the general public. These products are primarily for exterior and interior coatings for houses and buildings, although sizeable amounts of automobile and machinery refinishes, traffic paints and marine shelf-goods are also dispensed through trade sales outlets (Kline & Co., 1975).

Industrial product finishes or chemical coatings are produced to user specification and sold to other manufacturers for factory applications on such items as automobiles, aircraft, appliances, furniture and metal containers. They also include the category of industrial maintenance coatings, which are specially formulated and are used to maintain industrial plants and equipment (e.g., as resistance to corrosion). Within these major product lines, the paint industry produces thousands of different products for a broad spectrum of substrates, applications and customers (Kline & Co., 1975).

World production in 1971 of surface coatings by selected countries or regions is given in Table 6. North America was the largest producer and manufactured 4.5 million tonnes (31.6%), while western Europe produced 4.2 million tonnes (29.3%) and eastern Europe produced slightly over 3 million tonnes (21.6%; Kline & Co., 1975).

A more recent listing of paint production in the USA, Japan and western Europe is presented in Table 7. Japan is now the largest paint producer outside of the USA, followed by the Federal Republic of Germany, France, the UK and Italy. In 1986, US paint production was 967 million gallons [approximately 4340 thousand tonnes] (Reisch, 1987).

Estimated consumption of various resins, pigments and solvents in the USA in 1975, 1980 and 1985 is shown in Tables 8, 9 and 10. The major resins used in the production of paints are alkyd, acrylic and vinyl resins, which account for over 60% of total resin use in the USA. The main pigment was titanium dioxide and the major solvents aliphatic hydrocarbons, toluene and xylenes (see monographs, p. 125).

The number of paint manufacturers in the USA has declined steadily from about 1500 in 1963, to about 1300 in 1972 and 1000 in 1987 (Kline & Co., 1975; Layman, 1985; Reisch, 1987). In the UK, there have been similar reductions from about 500 paint manufacturers in the 1950s to only about 250–300 in 1985 (Layman, 1985).

Table 6. World production (in thousands of tonnes) of surface coatings by selected country or region in 1971^a

Region	Production	% Distribution
North America		
USA	4155	29.0
Canada	379	2.6
Total	4534	31.6
Europe		
Germany, Federal Republic of	1192	8.3
France	744	5.2
UK	614	4.3
Italy	420	2.9
Spain	207	1.4
Netherlands	192	1.3
Sweden	160	1.1
Belgium/Luxembourg	130	0.9
Austria	101	0.7
Denmark	84	0.6
Yugoslavia	80	0.5
Switzerland	68	0.5
Norway	66	0.5
Finland	46	0.3
Portugal	32	0.2
Turkey	27	0.2
Greece	20	0.1
Ireland	17	0.1
Total	4200	29.3
Eastern Europe (total)	3094	21.6
Asia		
Japan	1140	7.9
India	67	0.5
Israel	49	0.3
Hong Kong	26	0.2
Other ^b	304	2.1
Total	1586	11.1
Latin America^c	484	3.4
Oceania		
Australia	179	1.2
New Zealand	45	0.3
Other	4	<0.1
Total	228	1.6

Table 6 (contd)

Region	Production	% Distribution
Africa		
South Africa	81	0.6
Other	138	1.0
Total	219	1.5
TOTAL	14 345	100.0

^aFrom Kline & Co. (1975)^bIncludes the Philippines and the Republic of Korea^cIncludes Mexico**Table 7. Paint production (in thousands of tonnes) in selected countries in 1984^a**

Country	Production
USA ^b	4432
Japan ^c	1803
Germany, Federal Republic of	1321
France	809
UK ^d	670
Italy	625
Spain	278
Netherlands	253
Sweden	189
Denmark	133
Belgium	131
Austria	126
Portugal	92
Finland	82
Switzerland	82
Norway	75

^aFrom Layman (1985), unless otherwise specified^bFrom Connolly *et al.* (1986)^cFrom Kikukawa (1986)^dProduction in millions of litres

Table 8. Estimated consumption (in thousands of tonnes) of resins in paints and coatings in the USA^a

Resin	1975	1980	1985
Alkyd ^b	315	295	300
Acrylic	158	203	223
Vinyl	166	183	191
Epoxy ^c	38	70	87
Urethane	33	54	58
Amino	29	33	41
Cellulosic	24	27	24
Polyester ^b	11	33	62
Phenolic	11	11	12
Chlorinated rubber	6	8	8
Styrene-butadiene	11	7	6
Natural	9	8	7
Linseed oil	23	35	36
Other resins	77	61	66
Plasticizers	20	19	17
Total	931	1047	1138

^aFrom Connolly *et al.* (1986)^bData for 1985 are not comparable to those for previous years, since it is probable that some of the resins reported as alkyds in previous years were actually polyesters.^cIncludes unmodified epoxy resins plus hybrids (e.g., acrylate enhancement)**Table 9. Estimated consumption (in thousands of tonnes) of pigments in paints and coatings in the USA^a**

Use and pigment	1975	1980	1985
Colours			
Titanium dioxide	323	354	393
Chrome	29	33	33
Iron oxide	43	53	57
Carbon black	8	8	9
Other coloured inorganic	7	5	5
Phthalocyanine	1	2	2
Other organic	7	7	8
Aluminium	10	11	11
Fillers			
Calcium carbonate	175	175	213
Talc	136	150	136
Clay	154	159	199

Table 9 (contd)

Use and pigment	1975	1980	1985
Fillers (contd)			
Silica	59	71	83
Barytes	34	33	34
Nepheline syenite and feldspar	19	34	35
Other extenders and fillers	17	20	26
Other			
Zinc oxide	10	12	12
Zinc dust	24	32	24
Lead (corrosion inhibiting)	11	8	5
Cuprous oxide	2	4	3
Other	3	6	6
Total	1072	1177	1294

^aFrom Connolly *et al.* (1986)

Table 10. Estimated consumption (in thousands of tonnes) of solvents in paints and coatings in the USA^a

Solvent	1975	1980	1985
Aliphatic hydrocarbons	533	456	433
Toluene	281	265	277
Xylenes	240	213	211
Other aromatic compounds	91	79	84
Butyl alcohols	50	59	68
Ethyl alcohol	82	84	95
Isopropyl alcohol	48	53	41
Other alcohols	25	26	29
Acetone	79	79	89
Methyl ethyl ketone	145	154	152
Methyl isobutyl ketone	47	48	50
Ethyl acetate	31	35	36
Butyl acetates	55	62	71
Propyl acetates	8	8	9
Other ketones and esters	61	68	75
Ethylene glycol	23	29	34
Propylene glycol	14	12	14
Glycol ethers and ether esters	109	120	136
Chlorinated solvents	6	10	21
Miscellaneous	16	16	15
Total	1944	1876	1940

^aFrom Connolly *et al.* (1986)

2.2 Use

(a) *Uses and application methods*

The various uses of paint products are described by type of resin in Table 11.

Paints are applied by direct contact or by deposition by atomization processes. The direct-contact category includes the familiar brushing and roller techniques, dipping, flow coating and electrodeposition. Deposition by atomization processes includes conventional spray, hot spray and electrostatic spray. Machine roller coating is used in the industrial application of paint to paper, plywood and metal sheets, as well as continuous coating of metal coils. Dip coating is used in large industrial operations (Browne, 1983; Lowell, 1984).

Probably the greatest advance made during the early 1900s in the field of paint technology was the introduction of the spray gun. Its advent helped in the introduction of cellulose nitrate lacquers and their application to automobile assembly line production. Electrostatic spraying was first introduced in the USA in the 1940s and later in the UK. Electrodeposition of paint, introduced during the 1960s, is an important milestone in industrial painting and has proven especially advantageous for painting automobile bodies and other parts because of its superior corrosion resistance. In this technique, the coating is an aqueous dispersion of low solid content. The binder particles carry ionized functional groups which may be positive or negative, thus having either anodic or cathodic deposition. The anodic type typically uses amino- or alkali-solubilized polycarboxylic resins and the cathodic type, salts of amine-treated resins, such as epoxy resins (Brewer, 1984; Lowell, 1984).

(b) *Use patterns*

Use of paints in the major markets in the USA in 1985 is presented in Table 12. Distribution of use of resins and the other main components of paints in the USA in 1985 is shown in Table 13.

2.3 Exposures in the workplace

(a) *Introduction*

No data on the numbers of paint production workers or painters worldwide were available to the Working Group. According to a 5% census sample of the US population in 1970 (National Institute for Occupational Safety and Health, 1970), paint manufacturers employed approximately 62 000 workers. Extrapolating from the proportion of world production of surface coatings contributed by the USA (see Table 6), it can be estimated that the total number of paint production workers in the world is approximately 200 000. According to the same US census survey, there were 362 000 construction/maintenance painters and 106 000 painters/paperhangers/decorators in the USA. On the basis of these figures, it can be similarly estimated that the number of painters worldwide must be at least several million.

Table 11. Uses of polymer systems in industrial coatings^a

Polymer systems	Coil	Metal	Appli- ance	Furni- ture	Hard- board	Lumber and plywood	Marine	Mainte- nance	Auto- mobile manu- facture	Auto- mobile refinish	Tins	Paper- board
Natural and modified polymers												
Drying oils				+	+	+	+	+			+	
Cellulose esters		+		+		+			+	+		+
Cellulose ethers				+						+		
Condensation systems												
Alkyd resins	+	+	+	+	+	+	+	+	+	+	+	+
Polyesters, high molecular weight	+	+	+		+	+						
Amino resins	+	+	+	+	+	+			+	+		
Phenolic resins	+	+	+				+	+	+	+	+	
Polyamides		+					+	+			+	+
Polyurethanes				+	+		+	+	+		+	+
Epoxy resins	+	+	+	+	+		+	+	+		+	
Silicones		+	+				+	+			+	
Vinyl polymers and copolymers based on:												
Butadiene								+			+	
Acrylic or methacrylic ester	+	+	+	+	+		+	+	+	+	+	+
Vinyl acetate				+	+	+	+	+			+	
Vinyl chloride	+	+	+	+	+	+	+	+	+		+	
Vinylidene chloride							+	+			+	+
Styrene		+	+		+			+	+	+	+	+
Vinyl acetal or butyral	+	+		+				+			+	
Fluorocarbons	+											
Resin combinations												
Acrylic and amino	+	+	+	+	+				+		+	+
Acrylic and epoxy		+	+						+		+	
Acrylic and silicone	+	+						+				
Alkyd and amino	+	+	+	+	+				+	+	+	+
Alkyd and acrylic		+	+	+				+	+	+	+	
Alkyd and epoxy		+	+					+	+			
Alkyd and silicone	+	+	+									
Polyester and epoxy		+	+					+	+		+	+
Polyester and silicone	+	+			+							
Cellulose ester and urethane				+								
Alkyd, acrylic and amino					+							
Polyester and amino											+	+
Phenolic and epoxy							+	+			+	
Epoxy and amino											+	
Phenolic and amino											+	
Alkyd and vinyl chloride polymers							+	+				

^aFrom Lowell (1984)

Table 12. Consumption of paints and coatings by major market in the USA, 1985^a

Paints and coatings	%	% of total
Architectural coatings		46
Water-based	73	
Solvent-based	27	
Product finishes		38
Miscellaneous ^b	32	
Containers	15	
Wooden furniture	14	
Automotive	12	
Machinery	10	
Metal furniture	7	
Coils	5	
Wood flat stock	4	
Special purpose coatings		16
Traffic	28	
Auto refinishes	25	
Special maintenance	19	
Aerosols	10	
Other ^c	18	

^aFrom Connolly *et al.* (1986)^bIncludes appliances, other transportation, marine, paper and foil, and other^cIncludes paints for roofs, bridges, marine shelf goods, metals and others

A wide range of potential occupational health hazards is present in relation to the manufacture and use of paints, varnishes and lacquers. Coatings are complex mixtures containing a variety of groups of substances, such as organic solvents, organic and inorganic pigments, extenders, resins and additives such as catalysts, surfactants, driers, plasticizers and biocides. Each of these categories covers a range of tens or hundreds of individual chemical compounds (Connolly *et al.*, 1986). It has been reported that over 3000 individual paint components are used worldwide.

Occupational exposure results predominantly from the inhalation of gases and vapours, mainly organic, from solvents, binders and additives, of mainly inorganic pigment dusts and of complex inorganic and organic mixtures such as dusts from dried coatings and mists generated during the spraying of paint. The other major route of occupational exposure is through cutaneous contact with the various paint compounds, many of which can be absorbed through the skin. Ingestion related to personal work habits constitutes another potential route of entry.

Table 13. Distribution of use of components of paints in the USA in 1985^a

Use	Proportion by use (wt% of total)					Total (wt% of grand total)
	Resins	Pigments	Additives	Solvents	Water	
Product finishes						
Wood furniture and fixtures	25.7	2.9	0.1	66	5.3	4.4
Wood mat stock	38	20	0.6	24	17	1.7
Metal furniture and fixtures	32	25	0.1	36	6.7	2.8
Containers and closures	38	6.2	0.3	43	13	4.8
Sheet, strip and coil	32	26	0.1	33	8.1	2.3
Major appliances	37	24	0.1	33	5.4	1.4
Other appliances	39	22	0.1	35	3.5	0.8
Automobile						
Topcoat	32	16	0.05	46	5.7	1.7
Primer	23	24	0.3	29	23	1.7
Underbody components and parts	26	18	0.2	35	21	1.1
Trucks and buses	31	16	0.1	27	25	1.2
Railroad	25	25	0.1	33	17	0.4
Other transportation	38	25	neg	38	neg	0.4
Machinery and equipment	30	27	0.2	38	5	4.2
Electrical insulation	51	0.0	0.0	49	neg	1.1
Paper, film and foil	39	2	0.1	43	17	1.0
Other product finishes	27	17	0.2	40	16	5.2
Total	31	17	0.2	41	11	36.8
Architectural coatings						
Interior water-based						
Mat	14	40	2	1.6	43	16.5
Semigloss and gloss	18	23	2	9.5	48	4.5
Other	18	21	1.5	0.2	57	1.3
Interior solvent-based						
Mat	21	58	0.2	30	0.0	1.1
Semigloss and gloss	27	41	0.1	32	0.0	2.6
Varnish	33	1.4	0.2	27	0.0	0.7
Other	26	21	0.2	43	0.0	0.7
Exterior water-based						
Mat (house paints)	19	35	25	4.2	39	11.2
Trim	20	23	2.6	3.3	51	0.9
Stains	17	19	1.5	3.5	59	1.4
Other	17	24	1.7	5	52	0.8
Exterior solvent-based						
Mat (house paints)	28	38	0.5	33	0.0	2.1
Enamel	42	26	0.3	32	0.0	2.4
Primer	25	37	0.7	37	0.0	0.7
Varnish	58	0.0	0.4	42	0.0	0.3
Stains	41	0.0	0.4	59	0.0	1.2
Other	24	40	0.5	36	0.0	0.3
Total	20	33	1.7	12	33	48.5

Table 13 (contd)

Use	Proportion by use (wt% of total)					Total (wt% of grand total)
	Resins	Pigments	Additives	Solvents	Water	
Special-purpose coatings						
Maintenance	36	23	0.2	33	8.2	2.8
Marine						
Pleasure	50	0.0	0.5	50	0.0	0.04
Commercial and maintenance	35	29	0.1	35	0.5	1.1
Automobile refinishing	23	22	0.2	55	neg	3.2
Traffic paints	15	59	0.1	26	0.9	5.6
Aerosol	15	5.5	0.1	80	neg	1.1
Other	21	46	0.2	32	0.1	3.2
Total	23	38	0.1	37	1.8	16.4
Grand total (thousands of tonnes)	1138	1294	42	1217	884	4536

^aFrom Connolly *et al.* (1986); neg, negligible

Workers in the painting trades may also be exposed to a number of chemical agents originating from other operations that they or fellow workers are involved in, such as cleaning and preparing by chemical or mechanical means the object to be painted or cleaning themselves and the painting equipment.

The main substances to which workers may be exposed are listed in Table 14. The main occupational agents for which quantitative exposure data are available are presented in the following sections, covering the major paint trades.

Exposure to solvent mixtures is often described in the following sections using a summary measure, the cumulative exposure index (CEI), i.e., the sum of ratios of various measured levels to the respective occupational exposure limits. If this index exceeds unity, the combined exposure to different components of a solvent mixture is considered to exceed the recommended exposure limit. The values of the CEI are not always comparable because the exposure limits may vary with country and time.

In some painting operations, personal protective equipment is worn. However, it is common industrial hygiene practice to determine potential exposure by monitoring the breathing zone outside such protective gear. The results reported are thus not necessarily actual personal exposures.

Table 14. Main substances (and classes of substances) to which workers may be exposed in the painting trades^a

Material	Principal uses or sources of emissions	IARC Monographs ^b
Acrylates (e.g., ethyl acrylate, methyl methacrylate)	Acrylic resins, ultraviolet curing paints	IARC (1979c)
Acrylic resins	Binders	IARC (1979c)
Alcohols, aliphatic (e.g., methanol, isopropanol, <i>n</i> -butanol)	Solvents (lacquers), paint removers	
Alkalis (e.g., sodium hydroxide, potassium hydroxide)	Paint removers	
Alkyd resins	Binders	
Aluminium, powder	Pigment	
Amides, aliphatic (e.g., dimethylformamide)	Solvents	This volume
Amines (mono), aliphatic (e.g., diethylamine) and alkanolamines (e.g., 2-amino-2-methyl-1-propanol)	Water-based paints	
Amines (poly), aliphatic (e.g., diethylenetriamine)	Curing agents (epoxy resins)	
Amines, aromatic (e.g., <i>meta</i> -phenylenediamine, 4,4-methylenedianiline)	Curing agents (epoxy resins)	IARC (1978b) IARC (1986d)
Amino resins (e.g., urea-formaldehyde resins, melamine-formaldehyde resins)	Binders	IARC (1982a)
Ammonia	Water-based paints	
Anhydrides, organic (e.g., maleic anhydride, phthalic anhydride, trimellitic anhydride)	Alkyd resin synthesis, curing agents (epoxy resins)	
Antimony compounds (e.g., antimony trioxide)	Pigments, fire retardant pigments	This volume
Arsenic compounds (e.g., copper aceto-arsenate)	Antifouling agents	IARC (1980c)
Asbestos	Filler, spackling and taping compounds, talc	IARC (1977b)
Barium compounds (e.g., barium sulfate, barium carbonate)	Pigments	
Benzoyl peroxide	Catalyst	IARC (1985c)
Bisphenol A	Epoxy resins	
Cadmium compounds (e.g., cadmium sulfide, cadmium sulfoselenide)	Pigments	IARC (1976c)
Calcium compounds (e.g., calcium sulfate, calcium carbonate)	Fillers	
Camphor	Plasticizer	
Carbon black	Pigment	IARC (1984)
Cellulose ester resins (e.g., cellulose nitrate, cellulose acetate)	Binders	
Chloracetamide	Fungicide (water-based paints)	
Chromium compounds (e.g., chromic oxide, chromates)	Pigments	IARC (1980a)
Chlorofluorocarbons	Spray-can paint propellants	IARC (1986e)
Clays (e.g., bentonite)	Fillers	

Table 14 (contd)

Material	Principal uses or sources of emissions	IARC Monographs ^b
Coal-tar and asphalt	Special waterproof coatings (ships, tanks, pipes)	IARC (1985b)
Cobalt compounds	Pigments, driers	
Copper and copper compounds (e.g., bronze powder, cuprous oxide)	Pigments, antifouling agents	
Dyes and pigments, organic (e.g., aromatic azo dyes, phthalocyanines, rhodamine)	Pigments	IARC (1974b, 1978a)
Epichlorohydrin	Epoxy resins	IARC (1976b)
Epoxy resins	Binders	IARC (1976a)
Esters, aliphatic (e.g., ethyl acetate, isopropyl acetate)	Solvents	
Ethers, aliphatic (e.g., isopropyl ether, tetrahydrofuran) and glycol ethers (e.g., methylcellosolve)	Solvents	
Formaldehyde	Amino resin varnishes, biocide (water-based paints)	IARC (1982a)
Gasoline	Solvent	IARC (1989a)
Glycidyl ethers (e.g., <i>n</i> -butyl glycidyl ether and bisphenol A diglycidyl ether)	Epoxy resin diluents and constituents	This volume
Glycols (e.g., ethylene glycol)	Polyester resins, water-based paints	
Hydrocarbons, aliphatic (e.g., hexanes, heptanes)	Solvents (naphthas, white spirits)	
Hydrocarbons, aromatic (e.g., benzene, toluene, xylenes, trimethylbenzene)	Solvents (naphthas, white spirits), paint removers	IARC (1982b); this volume
Hydrocarbons, chlorinated (e.g., dichloromethane, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene)	Solvents, paint removers, metal degreasers	IARC (1979g,h,i; 1986c)
Hydrochloric acid (hydrogen chloride)	Catalyst (amino resins)	
Iron compounds (e.g., iron oxides, ferric ferrocyanide)	Pigments	IARC (1972)
Isocyanates (e.g., 1,6-hexamethylene diisocyanate, toluene diisocyanate)	Two-component polyurethane resins	IARC (1986b)
Isothiazolones (e.g., 1,2-benzisothiazolin-3-one)	Biocides in tinned foods	
Kerosene	Solvent	IARC (1989b)
Ketones, aliphatic (e.g., acetone, methyl ethyl ketone, cyclohexanone, isophorone, diacetone alcohol)	Solvents, lacquers, paint removers	
Lead compounds (e.g., lead chromate, lead oxides, basic lead carbonate, lead naphthenate)	Primers, pigments, driers	IARC (1980a)
Magnesium compounds (e.g., magnesium carbonate)	Fillers	
Manganese naphthenate	Drier	
Mercury compounds (e.g., mercuric oxide, phenyl mercuric acetate)	Fungicides (water-based paints)	
Methyl cellulose	Thickener (water-based paints)	

Table 14 (contd)

Material	Principal uses or sources of emissions	IARC Monographs ^b
Mica	Filler	
Molybdenum compounds (e.g., lead molybdate)	Pigments	
Nickel, metal powder	Pigment	IARC (1976c)
Nitroparaffins (e.g., nitroethane, 2-nitropropane)	Solvents	IARC (1982e)
Oils, vegetable (e.g., linseed oil, tung oil)	Binders	
Oximes (e.g., methyl ethyl ketoxime)	Anti-oxidants, anti-skinning agents	
Petroleum solvents (e.g., Stoddard solvent, VM & P naphtha)	Solvents, paint removers	This volume
Phenol	Phenol-formaldehyde resins, paint remover (formerly)	This volume
Phenol-formaldehyde resins	Binders	
Phenols, chlorinated (e.g., pentachlorophenol)	Fungicides (water-based paints)	IARC (1979j)
Phosphates, organic (e.g., tricresyl- <i>ortho</i> -phosphate, tributyl phosphate)	Plasticizers	
Phthalate esters (e.g., dibutyl phthalate, dioctyl phthalate)	Plasticizers	IARC (1982c)
Polychlorinated biphenyls	Plasticizers	IARC (1978c)
Polycyclic aromatic hydrocarbons	Special waterproof coatings (ships, tanks, pipes)	IARC (1983b)
Polyester resins	Binders	
Polyurethane resins	Binders	IARC (1979k)
Polyvinylacetate resins	Binders	IARC (1979b)
Pyrolysis fumes	Removal of paint by burning; heat-curing operations	
Rosin	Binder	
Rubber, synthetic (e.g., butyl rubber, styrene-butadiene rubber)	Binders (special paints, water-based paints)	IARC (1982f)
Shellac resin	Binder	
Silica, amorphous (e.g., diatomaceous earth)	Filler	IARC (1987b)
Silica, crystalline (e.g., quartz)	Filler, sand-blasting operation	IARC (1987b)
Silicates (e.g., sodium silicate, aluminium silicate)	Fillers	
Stearates (e.g., aluminium, zinc stearates)	Soaps, flattening agents	
Strontium compounds (e.g., strontium chromate, strontium sulfide)	Pigments	IARC (1980b)
Styrene	Polyester resins	IARC (1979d)
Styrene oxide	Diluent (epoxy resins)	IARC (1985d)
Sulfuric acid	Metal cleaner	
Talc	Filler	IARC (1987c)
Tin, metal powder	Lacquers (tinplate containers)	
Tin, organic compounds (e.g., tri- <i>n</i> -butyltin oxide, dibutyltin laurate)	Antifouling agents, catalysts	
Titanium dioxide	Pigment	This volume
<i>para</i> -Toluenesulfonic acid	Catalyst (amino resins)	
Turpentine	Solvent	

Table 14 (contd)

Material	Principal uses or sources of emissions	IARC Monographs ^b
Vinyl acetate	Polyvinylacetate resins	IARC (1986a)
Zinc and compounds (e.g., zinc metal powder, zinc oxide, zinc chromate)	Pigments, catalysts, bodying agents	IARC (1980b)

^aFrom Sterner (1941); Piper (1965); Phillips (1976); O'Brien & Hurley (1981); O'Neill (1981); Dufva (1982); Krivanek (1982); Ringen (1982); Adams (1983); Selikoff (1983); National Institute for Occupational Safety and Health (1984); Swedish Work Environment Fund (1987) and previous sections

^bSee also IARC Monographs Supplement 7

(b) *Manufacture of paints and related products*

The manufacture of paints and related products such as varnishes, lacquers, enamels and paint removers involves the handling and processing of a complex array of raw materials, e.g., pigments, extenders, solvents, binders and additives, described in section 1, implying overall potential worker exposure to hundreds of chemicals (National Institute for Occupational Safety and Health, 1984). Furthermore, raw materials are often subjected to chemical changes such as during polymerization and cooking, thus creating a variety of new hazards.

The potential for occupational exposure depends largely on the basic types of products being manufactured, the degree of automation of the manufacturing process, the availability of exposure control measures and the nature of the specific job held. Various job classification systems have been developed for the paint manufacturing industry. Workers have thus been regrouped according to the basic product made – water-based paints, solvent-based paints, lacquer and vehicle – and to functions – pre-batch assembler, mixer, tinter, filler, tank and tub cleaner, reactor operator, varnish cooker, filter press operator (Morgan *et al.*, 1981). Additional functions are raw materials handler, laboratory personnel and others such as packagers, maintenance personnel, shippers and warehouse workers (National Institute for Occupational Safety and Health, 1984).

Heavy exposures, both by inhalation and skin contact, occur specifically in operations that can involve manual handling procedures such as weighing dry ingredients (pigments, extenders, resins, additives), loading them into mixing equipment, adding solvents to mills, and cleaning equipment (mixers, mills, reactors, kettles, tanks, filters). Additional exposure to solvents occurs in thinning, tinting and shading procedures, filling operations and filtering of varnishes. The cooking of varnishes may produce emissions of various aldehydes such as acrolein, of phenol, ketones, glycerine and fatty acids as well as dusts or vapours of maleic, phthalic and fumaric anhydrides during the loading of kettles. The production of powder coatings can be associated with significant exposure to dust from resin powders, pigments, curing agents and other additives. In the manufacture of radiation-curable coatings, exposures may occur to monomers such as ethyl acrylate, other acrylates and photoinitiators. Caustic solutions may be used in the cleaning of dispersion equipment (National Institute for Occupational Safety and Health, 1984). In general, important opportunities for exposure

result from the presence of spills and the continuous spattering from machines (Adams, 1983).

(i) *Exposure to solvents*

Because of their volatility, solvents are ubiquitous air contaminants in paint manufacturing industries.

Exposure levels measured for various categories of workers in nine Swedish companies and reported as the sums of standardized concentrations are summarized in Table 15. High concentrations of solvents were found in all operations, the worst situation being manual cleaning of equipment with solvents. Local exhaust ventilation was common, and respirators were not often used. Of the 14 types of solvents monitored, the most common were xylene, toluene, butanol and esters (Ulfvarson, 1977).

Exposure to organic solvents was measured in the breathing zone of 17 Swedish male paint industry workers presumed to have the highest exposure of 47 workers employed in seven factories in Sweden, by collecting air with battery-driven syringes and analysing with two portable gas chromatographs. The median exposure values were (mg/m³): xylene, 111 (16 persons); toluene, 11 (16 persons); isobutanol, 5 (15 persons); ethylacetate, 20 (14 persons); *n*-butylacetate, 14 (13 persons); ethanol, 13 (13 persons); *n*-butanol, 7 (13 persons); methylacetate, 12 (eight persons); dichloromethane, 719 (three persons); white spirits, 45 (three persons); and isopropanol, 129 (one person) (Haglund *et al.*, 1980).

Overall solvent exposure of workers known to be exposed to toluene was measured in seven paint manufacturing companies in New Zealand. Mean total levels of solvents ranged from 19 ppm in one company (five workers sampled) to 130 ppm in another one (three workers sampled), with individual values ranging from 7 to 297 ppm. Toluene, xylene and ethylbenzene were found in the atmosphere of all seven plants; the frequencies of other solvents were as follows: heptane, 6/7; *n*-hexane and methylethylketone, 5/7; acetone, 4/7; pentane, methylisobutylketone, ethanol and *n*-butylacetate, 3/7; and isopropanol, 1/7 (Winchester & Madjar, 1986).

In another study in Sweden, 47 employees of seven paint manufacturing industries, known to be exposed to solvents and including nine manual cleaners of paint mixing equipment, were surveyed for exposure to 12 solvents. The results are summarized in Table 16. The main exposures with regard to both frequency and weight were to xylene and toluene. Outstandingly high exposures occurred during the manual cleaning of equipment (Lundberg & Håkansson, 1985).

In a study on the effects of long-term exposure to solvents in the paint industry in Sweden, overall solvent exposure in a large paint manufacturing company was estimated for various work tasks over three historical periods. The results are presented in Table 17 in terms of the CEI, i.e., the sum of the ratios of the various exposure levels to the respective Swedish occupational standards in 1982 for the various solvents (Ørbaek *et al.*, 1985).

Table 15. Exposure levels (personal breathing-zone samples) to combined organic solvents during various paint manufacturing operations^a

Operation	Sampling condition		Combined exposure ^b		Main solvents ^c	No. of samples in which solvent found
	No. of samples	Sampling time (min)	Mean	Range		
Charging solvents	33	4-43	2.0	0.2-16	Xylene	16
					Mesitylene	4
					Toluene	4
					Styrene	2
					Butanol	9
Pigment dispersion	18	9-66	1.5	0.2-4.4	Xylene	13
					Butanol	4
Tinting, thinning	14	15-32	0.9	0.1-2.0	Xylene	11
					Butanol	3
Can filling, paints	39	11-32	1.3	0.02-6.6	Xylene	23
					Alkanes	4
					Butanol	7
					Benzene	4
					Toluene	6
Can filling, thinners	14	9-20	1.8	0.1-7.4	Toluene	3
					Xylene	5
					Trichloroethylene	3
					Esters	2
					Acetone	1
Manual cleaning of equipment with solvents	51	3-28	5.7	0.5-30	Xylene	33
					Butanol	8
					Toluene	13
					Dichloromethane	9
					Esters	7
					Ketones	4

^aFrom Ulfvarson (1977)^bSum of ratios of individual solvent levels to their occupational exposure limits^cSolvents constituting at least one-fifth of individual combined exposure levels

The overall improvement in exposure levels over time has been attributed in large part to better control measures and to the increasing production of water-based paints. These results are corroborated by other estimates of the evolution of average solvent exposures in the Swedish paint manufacturing industry with the following values for the overall CEI: 2 in 1950-69, 1.5 in 1970-74, 0.7 in 1975-79 and 0.3 since 1980 (Lundberg, 1986). Heavy naphthas, toluene and benzene are reported to have been the most commonly used solvents during the 1930s, presumably with high exposure levels. Substitutes for aromatic hydrocarbons,

Table 16. Exposure levels (8-h time-weighted average) to organic solvents of 47 paint manufacturing workers^a

Solvent	No. exposed	Exposure (mg/m ³)	
		Median	Range
Xylene	44	82	1-6070
Toluene	43	10	1-1260
Isobutanol	36	4	1-1040
n-Butanol	35	6	1-1540
Ethanol	33	12	1-1090
Ethyl acetate	32	26	1-767
n-Butyl acetate	31	9	1-1680
White spirits	18	44	5-74
Methyl acetate	11	13	3-169
Dichloromethane	5	719	10-2420
Methyl ethyl ketone	5	39	8-124
Isopropanol	3	129	6-258

^aFrom Lundberg & Håkansson (1985)**Table 17. Average combined organic solvent exposure^a of paint industry workers in various work areas over three periods^b**

Work area	Period		
	1969 and earlier	1970-75	1976 and later
Industrial paint section			
Mixing	2	1.3	0.7
Grinding	3	1.8	0.9
Tinting-finish	2.2	1.5	0.6
Tapping	2.2	1.2	0.6
Cleaning of vessels	4.5	3	1.5
Alkyd paint section (mixing, tinting, tapping)			0.1-0.2
Small batch manufacturing		1.4	0.7
Filler manufacturing	0.2	0.15	0.1
Storage	0.2	0.15	0.1
Cellulose paint section	2.5		
Laboratory			
Product development	0.7	0.4	0.15
Control laboratory	1	0.75	0.4
Process engineering	2	1	0.4

^aSum of ratios of individual solvent levels to their occupational exposure limits; solvents considered: acetone, butanol, butylacetate, ethanol, ethyl acetate, white spirits, methyl isobutyl ketone, toluene and xylene^bFrom Ørbaek *et al.* (1985)

including turpentine, decaline and tetraline, would have been used during the Second World War and immediately after. From 1950 until today, the most commonly used solvents would have been xylene, toluene, white spirits, ethanol, butanol, ethyl acetate and butyl acetate. While operations were largely manual before the late 1960s, improvements such as local exhaust ventilation were gradually introduced in the mid-1960s.

(ii) *Exposure to dusts*

In a Swedish investigation covering ten factories manufacturing paint and industrial coatings, dust was found during tinting, handling of bags, compressing empty bags, floor cleaning and emptying air-cleaner filters. The principal exposure to dust, however, was found during charging of raw materials. Sixty-one breathing-zone samples taken over durations of 5 min to 8 h indicated total dust exposure levels of 1.7–70 mg/m³. Raw materials charged included inorganic and organic pigments and fillers, chromium and lead compounds, talc and silica. The highest total dust levels (range, 7.7–70 mg/m³; four samples) were found in a powder coatings factory. Local exhaust ventilation was widely used, but fewer than half of the workers wore respirators. A few air samples were obtained to evaluate exposure to specific dusts during charging operation in some of the companies. Quartz was measured in five factories, with levels ranging from 0.01 to 0.9 mg/m³. Asbestos levels ranged from 0.3 to 5 fibres/cm³ (four factories). Chromium levels (as CrO₃) ranged from 0.003 to 1.6 mg/m³ (seven factories), while lead levels ranged from 0.006 to 4 mg/m³ (three factories; Ulfvarson, 1977). Blood lead concentrations monitored in 80 workers in 12 paint manufacturing companies in Finland were 5–72 µg/100 ml. The highest value was found in a spray painter (Tola *et al.*, 1976).

(iii) *Other exposures*

Exposure to ammonia was reported while charging it for use in water-based paints in the Swedish paint industry, at average levels of 50–80 ppm (35–56 mg/m³). In one case, more than 700 ppm (490 mg/m³) was measured. The levels of pentachlorophenol and phthalic anhydride were below the standards of 0.5 mg/m³ and 2 ppm (12 mg/m³), respectively (Ulfvarson, 1977). The concentration of diethylene triamine was below the detection limit (0.01 mg/m³) in the breathing zone of two workers canning epoxy paint curing agents in a Finnish paint factory (Bäck & Saarinen, 1986).

In a US paint manufacturing company, the 8-h time-weighted average (TWA) concentration of vinyl acetate ranged from 1.0 to 8.4 ppm (3.6–30.6 mg/m³; four samples). Personal and area air samples indicated concentrations of ethyl acrylate ranging from below the limit of detection to 5.8 ppm (23.8 mg/m³); concentrations of butyl acetate were all below the limit of detection (16 samples), except one sample at 0.9 ppm (4.7 mg/m³; Belanger & Coye, 1980).

(c) *Construction painting and lacquering*

Usual painters' work in the construction industry involves the use of a rather limited number of types of coatings – mainly decorative water- or solvent-based paints and wood lacquers and varnishes. The potential for exposure to a variety of substances (mainly solvents and pigments) is high, however: painting performed inside buildings, where poor ventilation opportunities, especially in confined spaces such as small rooms, cupboards, bath-

rooms, can lead to very high levels of contaminants; whereas when painting the outside of buildings (facades, windows, roofs), natural ventilation is usually effective. Painting of new buildings usually involves mainly water-based paints and spraying equipment; however, during renovation or maintenance, solvent-based paints are still widely used and work is usually performed by hand with a brush or roller.

Surfaces to be coated can be made of plaster- or gypsum-based wall-board composite materials, concrete, wood such as for windows, doors and flooring, and more rarely metal. Construction painters may spend a good proportion of their time in preparatory or accessory work. In a Finnish study on construction painters, 92 of 231 (40%) painters estimated that they spent more time on such work than actually painting (Riala *et al.*, 1984). Removing old paint and preparing surfaces in general may involve the use of paint strippers containing solvents such as dichloromethane, of gas-operated blow torch units or hot air guns which may generate organic pyrolysis fumes, metallic fumes and dusts from pigments containing *inter alia* chromium, lead and arsenic compounds. Other accessory tasks may be polishing, sanding or sandblasting operations, which generate old paint, quartz, concrete, plaster, wood and metal dusts. Acid or alkali washing solutions may be used, as well as steam generators for removing wallpaper, which release carbon monoxide-containing exhaust gases. Preparing surfaces also often involves filling cracks and holes using plaster, cement, sealers, spackling, taping and dry wall materials, putties and wood fillers, implying possible additional exposure to inorganic dusts and fibres (including asbestos) and solvents. Further exposure stems from the use of solvents during the cleaning of equipment as well as for personal cleaning (Ringen, 1982; Huré, 1986; Swedish Work Environment Fund, 1987).

The use of solvents in construction paints, and thus painters' exposures, has evolved radically with time. Early whitewashes and distempers contained no organic solvent, and oil paints contained only about 10% turpentine or, later, white spirits. Alkyd paints introduced in the 1960s required approximately 50% of a solvent such as white spirits. With the introduction of epoxy paints for special surfaces such as floors, other solvents such as alcohols, esters and aromatic hydrocarbons became more widely used. Water-based latex paints were introduced in the 1950s but were more widely accepted in the 1960s and 1970s, to become predominant in the 1980s; now, an estimated 60–80% of building trade coatings are water-based (Dufva, 1982; Hansen, 1982; Riala *et al.*, 1984). Vinylic and acrylic water-based paints are the most common, and these contain only a small percentage of organic solvents, mainly alcohols or glycol ethers.

The 8-h TWA exposure to solvents of 45 Dutch maintenance painters working on 12 different projects has been measured. Summed air concentrations averaged 101 mg/m³ (geometric mean) for the whole group and 59 mg/m³ for a subgroup of 20 house painters who applied only alkyd resins by brush and roller. Benzene was detected at only two of the sites and at low concentrations (up to 0.2 mg/m³). Toluene concentrations were below 4 mg/m³, except at one site where it reached 43 mg/m³. C₂- and C₃-substituted benzenes and C₈-C₁₁ alkanes were found at most sites, originating mainly from the use of white spirits. Workers using chlororubber paint in a pumping station were exposed to carbon tetrachloride at levels

ranging from 10 to 17 mg/m³; the highest level of toluene was also found at this site (Scheffers *et al.*, 1985).

The exposure of Danish house painters to 13 solvents was investigated in 1974. Overall exposure, standardized to relevant occupational exposure limits, was above the permissible limit for five of 11 maximal values, reaching up to 34 times the permissible limit. Individual solvent average exposure levels were especially elevated for benzene (55 ppm [175 mg/m³]; 41 samples), believed to originate from thinners, and for trichloroethylene (91 ppm [490 mg/m³]; 33 samples). The origin of the trichloroethylene was not specified (Mølhave & Lajer, 1976).

In Finland, concentrations of Stoddard solvent during application of solvent-containing alkyd paints were 22–65 ppm (seven samples) and those during application of wood preservatives or alkyd varnishes, 68–280 (four samples). The overall solvent CEI during parquet floor varnishing using cellulose nitrate lacquers and urea-formaldehyde varnish ranged from 0.6 to 2.3, according to Finnish occupational exposure limits. Acetone, ethanol, isobutanol and butyl acetate were the main solvents used. Exposure to formaldehyde during varnishing averaged 2.8–4.5 ppm (3.4–5.5 mg/m³; Riala, 1982). The risk of formation of bis(chloromethyl)ether (see IARC, 1987s) from the reaction between formaldehyde and hydrochloric acid (used as a hardener) in urea-formaldehyde varnishes has been evoked (Dufva, 1982), but levels higher than 0.2 ppb (>0.9 µg/m³) have not been found (O'Neill, 1981).

In a study in Finland mainly of maintenance construction workers, the overall average airborne concentration of solvents during alkyd and urethane painting and varnishing, expressed as solvent naphtha exposure, was 132 ppm (77 samples); this was much higher when there was no ventilation, either natural or artificial (197 ppm; 46 samples), than with ventilation (38 ppm; 31 samples). Highest concentrations were observed during painting in small, unventilated rooms (303 ppm) and on large surfaces such as walls and ceilings with no ventilation (206 ppm with roller and brush painting and 243 ppm with spray painting). Taking into account other activities, e.g., use of water-based paints, the overall average 8-h TWA exposure level was 40 ppm (Riala *et al.*, 1984).

Air concentrations (mg/m³) of organic vapours generated during the application of water-based paints were measured by personal sampling in Denmark, as follows: butyl acrylate, 0–2; diethylene glycol butyl ether, 4–5; diethylene glycol methyl ether, 8–32; dipropylene glycol methyl ether, 30–40; ethylene glycol butyl ether, 2–60; ethylene glycol phenyl ether, 0–0.7; propylene glycol, 2–70; 2,2,4-trimethylpentane-1,3 diol monoisobutyrate, 0.5–12; triethylamine, 4–6; and white spirits, 40–75. Concentrations of two gases, formaldehyde (at 0–0.4 mg/m³) and ammonia (at 2–12 mg/m³) were also reported (Hansen *et al.*, 1987).

In a Swedish study of renovation spray painters, very high concentrations of white spirits (1200–1500 ppm) were measured during use of alkyd-type paints and 100–1000-times lower concentrations of solvents during use of acrylate-polyvinyl acetate-based water-borne paints. Dust concentrations, originating from paint mist, were higher during use of water-based paints (77–110 mg/m³) than solvent-based paints (17–27 mg/m³). Inorganic substances were found to represent 80% and 70–85% of the dust content, respectively. Exposures to

substances such as lead (in solvent-based paints) and zinc (in both types of paints) were 10–23% and 1–2% of their respective exposure limits (Bobjer & Knave, 1977).

The mean blood lead level measured in 1962 for a group of 107 decorative and house painters in the USA was 23 $\mu\text{g}/100\text{ g}$ blood, similar to that in control groups (Siegel, 1963).

(d) *Painting, varnishing and lacquering in the wood industry*

Application of clear varnish or lacquer finishes on furniture represents the main use of coatings in the wood industry. Paints, varnishes and lacquers are also used in the production of various wooden raw materials (e.g., composite wood boards) and miscellaneous wooden articles (e.g., toys, tableware). Until the mid-1950s, cellulose ester-type lacquers were almost the only ones used in the furniture industry; however, amino resin-based, polyurethane and polyester coatings now constitute the main coatings in the industry (Swedish Work Environment Fund, 1987).

Workers are exposed mainly through inhalation or cutaneous absorption of solvents either from paint mist or from vapours generated by spraying operations, from vapours evolved from finished products or from auxiliary work such as mixing the coatings, cleaning equipment or applying other products such as wood fillers and sealants. The amount of exposure is influenced by the method of applying coatings; the most common are spraying, usually at low pressure, curtain and roller coating and dipping. The main categories of solvents used are aliphatic esters, ketones, alcohols and hydrocarbons as well as aromatic hydrocarbons (O'Brien & Hurley, 1981; Swedish Work Environment Fund, 1987).

Low molecular-weight resin constituents such as formaldehyde and isocyanates may be evolved during application or curing of coatings. Another possible exposure is to wood dust from the general factory environment and from preparatory work such as sanding.

Air monitoring was carried out over a ten-year period (1975–84) in 50 Finnish furniture factories, where the main coatings used were acid-cured amino resin-based paints and varnishes. The most commonly used solvents were xylene, *n*-butanol, toluene, ethanol, butylacetate and ethylacetate, which were present in more than 50% of 394 measurements. Mean concentrations of the solvents present were below 20 ppm, except for white spirits, which occurred at 66 ppm. Arithmetic mean solvent vapour concentrations measured during different work tasks ranged from 0.4 ppm in spray painting to 2.1 ppm during cleaning of a painting machine, with individual values varying from 0.1 to 7.4 ppm. Formaldehyde, derived from the amino resin binder, was the object of 161 short-term measurements (15–30 min) covering different work tasks. The arithmetic mean of the concentrations varied from 0.9 to 1.5 ppm (1.1–1.8 mg/m^3), with individual values ranging from 0.1 to 6.1 ppm (1.2–7.5 mg/m^3 ; Priha *et al.*, 1986).

The 8-h TWA exposure to formaldehyde of 38 employees in a Swedish light furniture factory applying acid-hardening clear varnishes and paints was found to average 0.4 mg/m^3 (range, 0.1–1.3) with a mean exposure to peak values (15 min) of 0.7 mg/m^3 . Mean exposure to solvents was low. The dust concentration was low – usually less than one-tenth of the Swedish threshold limit value of 5 mg/m^3 (Alexandersson & Hedenstierna, 1988).

In a study of a US wood furniture company producing stereo equipment cabinets, the solvent exposure of 27 employees in spray painting and finish wiping operations was mea-

sured. In spraying jobs that involved the use of an acrylic base coat, an oil-based glaze or stain and cellulose nitrate lacquers, total exposure to paint mist (8-h TWA) varied from 0.1 to 2.5 mg/m³ (geometric means). Combined exposure to solvents (CEI) varied from 0.05 to 0.11 in base coat operations (solvents measured: methyl ethyl ketone, isopropyl acetate, xylene, isopropanol, methyl isobutyl ketone, toluene and isobutyl isobutyrate), from 0.06 to 0.10 in glaze operations (toluene, xylene, ethylene glycol monobutyl ether and petroleum distillates) and from 0.08 to 0.24 in lacquer operations (isopropanol, ethanol, isophorone, isobutyl acetate, *n*-butanol, toluene, xylene, ethylene glycol monobutyl ether, methyl ethyl ketone, isobutyl isobutyrate, isopropyl acetate and petroleum distillates). The overall low air concentrations of paint mist and organic solvents were attributed to adequate ventilation in paint booths and good working practices (O'Brien & Hurley, 1981).

Exposure to organic solvent vapours was also measured in 16 small-scale industries in Japan, where synthetic *urushi* lacquer was applied to wooden tableware (bowls), vases and altars, and in two furniture factories. Work involved mainly brush painting, screen painting and hand-spraying operations. Toluene, xylene, ethylbenzene and *n*-hexane were the recorded solvents. Average mixed solvent personal exposure (CEI) was always low (below 0.44), except in the case of an automated spray operation (1.4; Ikeda *et al.*, 1985).

The average 4-h exposure to toluene of 20 workers employed in painting and hand-finishing in an Italian art furniture factory was 27–182 mg/m³. Toluene was the principal solvent found in the work environment; other major solvents found were acetone, isobutanol, ethanol and ethyl acetate (Apostoli *et al.*, 1982).

In the Finnish plywood industry, solvent concentrations in workroom air were recorded during coating operations involving polyurethane and alkyd paints. The following ranges in ppm (mg/m³) were obtained from eight to 12 measurements: (i) polyurethane paint: methyl isobutyl ketone, 2–28 (8.2–115); butylacetate, 8–50 (38–238); xylene, 10–25 (43–108); and cyclohexane, 1–28 (3.4–95); (ii) alkyd paint: toluene, 2–3 (7.5–11.3); xylene, 7–12 (30.4–52); isobutanol, 7–11 (21–33); and trimethylbenzene, 1–9 (5–44; Kauppinen, 1986).

In a US plant where paint was stripped from wood and metal, breathing zone TWA concentrations of dichloromethane for three operators ranged from 633 to 1017 mg/m³ in seven samples (Chrostek, 1980).

(e) *Painting in the metal industry*

Protection from corrosion is the primary aim of metal painting. Mild steel is thus almost always subjected to the application of a primer coat containing corrosion inhibitors such as iron and lead oxides or of zinc powder, further covered with a decorative paint. Aluminium may be covered with a zinc chromate-based primer before a decorative coat is applied.

During the preparation of metal parts, painters may be exposed to cleaning and degreasing agents, such as solvents, alkalis and acids, and to abrasive dusts, such as crystalline silica generated during blast cleaning. Depending on the industry, metal painters may be exposed to a variety of dusts, solvents, fumes and gases resulting from operations such as mixing paints, maintaining equipment, applying fillers, sealers or putty, or background metal welding or assembling operations. Most coatings used in the metal industry are solvent-based, and spray painting is the main method of application, leading to potential exposures to

paint mist and solvents. Two-component paints, such as those based on epoxy and polyurethane resins, play a major role, implying potential exposure to reactive substances such as isocyanates and epoxides. Air-drying or baking after application results in the evolution of solvents and, possibly, thermal degradation products of resins (Peterson, 1984).

(i) *Exposure to organic solvents*

Exposure of metal spray painters to a variety of solvents has been measured by the US National Institute for Occupational Safety and Health in a number of industries. The results are summarized in Table 18. Except in railroad car painting, overall exposure levels were found to be low. Toluene, xylene and petroleum distillates were among the most common solvents. Analyses of bulk air samples indicated no detectable benzene (O'Brien & Hurley, 1981).

In Finland, solvent concentrations were measured in the breathing zone of 40 car painters at six garages (54 1-h samples). Mean concentrations and the upper limits of various solvents were as follows (ppm) [mg/m³]: toluene, 30.6 (249) [115 (940)]; xylene, 5.8 (36) [25 (156)]; butylacetate, 6.8 (128) [32 (608)]; white spirits, 4.9 (150); methyl isobutyl ketone, 1.7 (39) [7 (160)]; isopropanol, 2.9 (85) [7 (209)]; ethyl acetate, 2.6 (14) [9 (50)]; acetone, 3.1 (25) [60]; and ethanol, 2.9 (27) [6 (51)] (Husman, 1980).

A large study of Swedish car refinishing workshops showed that painters spent only 15% of their time actually spray painting, the rest being occupied with grinding, filling, masking and assembling activities (60%) and colour mixing, degreasing and cleaning activities (25%). The highest overall solvent exposure was observed during spray painting, with a combined exposure of 0.3 (CEI; 106 samples). Toluene, xylene and ethyl acetate were present in all samples, at average levels of 39, 14 and 11 mg/m³, respectively. Ethanol, butanol and butyl acetate were observed at very low levels in nearly half the samples. Other solvents encountered frequently in other activities, although at low levels, included styrene and white spirits. A reconstitution of working conditions in 1955 indicated that exposure levels to solvents were higher than in 1975, which was considered to be representative of the 1960s and 1970s. In particular, when benzene was used as a solvent in 1975-77, the combined exposure (CEI) reached 0.8 (Elofsson *et al.*, 1980).

Breathing zone samples were taken during short-term spray painting operations in a small autobody repair shop in the USA. Elevated levels of total hydrocarbons (up to 1400 ppm) were measured in winter when the spraybooth fan was turned off to conserve heat. Under these conditions, high concentrations of toluene (590 ppm; 2224 mg/m³) were seen during lacquer spray painting and of xylene (230 ppm; 1000 mg/m³) and benzene (11 ppm; 35 mg/m³) during enamel spray painting. Summer conditions, when the fan was on, resulted in maximal concentrations of 330 ppm total hydrocarbons, 56 ppm (211 mg/m³) toluene, 44 ppm (191 mg/m³) xylene and 3.7 ppm (12 mg/m³) benzene. Other major solvents measured were acetone, cellosolve acetate, methyl isobutyl ketone, *n*-hexane, methyl cellosolve acetate, trimethylbenzene, ethylbenzene and *n*-butyl acetate (Jayjock & Levin, 1984).

Table 18. Painters' time-weighted average exposure levels (personal breathing-zone samples) in various metal spray-painting operations^a

Operation	Sampling time	No. of samples	Combined exposure ^{b,c}	Main solvents measured	Concentration (mg/m ³) ^c
Light aircraft finishing, primer spraying	25-41 min	3	0.9 ± 1.5	2-Butanone	42 ± 2.1
				Toluene	60 ± 1.2
				Ethanol	26 ± 1.6
				Isopropanol	19 ± 1.6
Light aircraft finishing, topcoat spraying	27-62 min	7	0.15 ± 1.3	Ethylacetate	77 ± 1.3
				Ethoxyethylacetate	44 ± 1.4
				Aliphatic hydrocarbons	34 ± 1.2
Light aircraft finishing, stripping operations	19-35 min	6	0.13 ± 2.5	Ethylacetate	52 ± 2.5
				Ethoxyethylacetate	30 ± 2.7
				Aliphatic hydrocarbons	73 ± 1.5
Car refinishing	15-45 min	7	0.09 ± 1.5	Toluene	39 ± 1.6
				Xylene	10 ± 1.0
				Petroleum distillates	21-63
				Other solvents	<10
Railroad car	15-60 min	14	1.3 ± 1.4	Toluene	188 ± 1.5
				Xylene	14 ± 2.6
				Other aromatic compounds	217 ± 1.4
				Aliphatic hydrocarbons	840 ± 1.4
Heavy equipment	60 min	12	0.01-0.05	Refined solvents	21-96
				Other solvents	≤5
Metal furniture, solvent and water-borne paints	8 h	5 painters	0.10-0.46	Toluene	12-61
				Xylene	7-48
				<i>n</i> -Butyl acetate	22-109
				Diisobutyl ketone	<1-23
				2-Ethoxyethyl acetate	1-14
				Aliphatic hydrocarbons	33-180
Metal furniture, high-solids paints	8 h	6 painters	0.07-0.31	Xylene	6-55
				Aromatic distillates	5-60
				Other solvents	<10
Appliance finishing	8 h	4 painters	0.38-0.79	Toluene	88-204
				Xylene	112-225

^aFrom O'Brien & Hurley (1981)^bCumulative exposure index (see p. 366), based on US Occupational Safety and Health Administration permissible exposure levels^cGeometric means ± geometric standard deviation, unless otherwise stated

In Japan, the full-shift TWA concentrations of the following solvents measured for 13 car repair painters (ppm [mg/m^3]; mean \pm standard deviation) were: xylene, 8 ± 8 [35 ± 35]; toluene, 19 ± 13 [72 ± 49]; isobutanol, 5 ± 5 [15 ± 15]; and ethyl acetate, 6 ± 4 [22 ± 14]. The overall combined exposure (CEI) was 0.38 ± 0.25 . Short-term samples taken during painting showed a higher combined exposure for ten of 14 workers, toluene being the major solvent encountered (Takeuchi *et al.*, 1982). In another Japanese study of car refinishing painters, high toluene concentrations were observed during painting in side-wall ventilated booths (410–660 ppm; 1546–2488 mg/m^3), compared with those in downdraft ventilated booths (28–87 ppm; 106–328 mg/m^3). Short actual painting periods resulted in full-shift TWA concentrations of organic solvents (toluene, xylene, methyl acetate, ethyl acetate and butyl acetate) below the exposure limits. The average hippuric acid concentration in the urine of painters (0.33 mg/ml) was slightly higher than that in controls (0.19 mg/ml ; Matsunaga *et al.*, 1983).

Exposure to toluene was investigated in 1940–41 in 106 painters in a large US airplane factory. Eight-hour TWA levels of toluene ranged from 100 to 1100 ppm (377–4147 mg/m^3); approximately 60% of workers were exposed to 200 ppm (754 mg/m^3) or more. Toluene was a major constituent of zinc chromate primers, lacquers, cellulose nitrate dope (lacquer) and brush wash (Greenburg *et al.*, 1942).

An industrial hygiene evaluation was conducted at a commercial airline maintenance facility in the USA. Employees working in and around jet aircraft during the paint stripping process were exposed to levels of dichloromethane in the breathing zone that ranged from 79 to 950 mg/m^3 with a mean of 393 mg/m^3 . During application of the prime coat, exposure to solvents was as follows (mg/m^3 ; mean and range): toluene, 112 (51–179); methyl ethyl ketone, 39 (8–77); butyl acetate, 72 (29–130); *n*-butanol, 25 (9–47); isopropanol, 51 (undetectable to 132); and cyclohexanone 10 (undetectable to 23). During application of the top coat, exposure to the solvents was: ethyl acetate, 333 (undetectable to 857); methyl ethyl ketone, 69 (undetectable to 219); methyl isobutyl ketone, 44 (nondetectable to 117); butyl acetate, 80 (undetectable to 210); xylene, 21 (undetectable to 49) and cellosolve acetate, 18 (undetectable to 46; Okawa & Keith, 1977).

Another study involved workers spray painting large commercial aircraft. Industrial hygiene measurements indicated short-term personal exposures as follows (mg/m^3 ; mean and range): toluene, 583 (140–1230); methyl ethyl ketone, 1436 (240–3250); ethyl acetate, 1231 (160–3520); naphtha, 44 (20–120); butyl acetate, 64 (20–150); xylene, 318 (60–1330); cellosolve acetate, 4843 (670–25 170); and dichloromethane, 654 (undetectable to 2840). Long-term exposures to the solvents were: ethyl acetate, 264 (10–1100); methyl ethyl ketone, 197 (20–440); toluene, 162 (30–450); butyl acetate, 11 (undetectable to 50); naphtha, 10 (undetectable to 160); xylene, 69 (10–270); cellosolve acetate, 640 (70–2490); and dichloromethane, 100 (undetectable to 760; Hervin & Thoburn, 1975).

Airborne concentrations (CEI) of solvent mixtures for jobs as paint mixer and spray painter ranged from 0.03 to 0.32 at a US plant manufacturing school and general purpose buses. The solvents found at the plant were petroleum naphtha, toluene, xylene, benzene, methyl ethyl ketone and *n*-hexane (Zey & Aw, 1984).

UK shipyard painters working in ships' accommodation and bilges were exposed to various mean TWA levels of organic solvents, depending on their job: 125 mg/m³ for three painters using a chlorinated rubber paint with white spirits as solvent, 215 mg/m³ for a worker using paint stripper with dichloromethane as the main solvent and 577 mg/m³ for four men using white interior paint with white spirits as the main solvent. Other paint solvents used frequently in dockyards are methyl-*n*-butyl ketone, *n*-butanol, trichloroethylene, xylene and cellosolve (Cherry *et al.*, 1985).

In Poland, phenol and hippuric acids were measured in 51 urine samples from shipyard painters working in small spaces of superstructures and in large holds. The average values of phenol in urine were 12.4–66.4 mg/l compared to 7.9 mg/l on average for a control group. Urinary phenol was attributed to benzene: the benzene concentration in air ranged from undetectable to 11 ppm (35 mg/m³). The average concentrations of hippuric acids in urine (sum of hippuric and methylhippuric acids) were 1812–5500 mg/l compared to 790 mg/l in a control group. Concentrations of toluene and xylene in air were 7–88 ppm (26–332 mg/m³) and 23–538 ppm (100–2335 mg/m³), respectively (Mikulski *et al.*, 1972). Elevated values of hippuric (up to 6700 mg/l) and methylhippuric acids (up to 7100 mg/l) were also measured in the urine of shipyard workers in Japan (Ogata *et al.*, 1971).

In a factory producing dump-truck bodies and earth-moving machinery in the UK, full-shift personal exposure levels to xylene and white spirits (two samples) were measured as 52 and 65 ppm (226 and 282 mg/m³) xylene and 7 and 12 ppm white spirits. After ventilation was properly adjusted, these levels dropped to 9 and 7 ppm (39 and 30 mg/m³) xylene and < 5 ppm white spirits (Bradley & Bodsworth, 1983). At a US plant where truck bodies and refuse handling equipment were manufactured, breathing zone concentrations of xylene during spray painting operations (eight samples varying from 1 to 3 h) ranged from 5 to 140 ppm (22–608 mg/m³; Vandervort & Cromer, 1975). Low exposure levels of toluene (3–18 mg/m³) and isobutyl acetate (2–44 mg/m³) were observed for Swedish spray painters in a plant manufacturing fireplaces (Hellquist *et al.*, 1983).

(ii) *Exposure to paint mists, dusts and specific metals*

Exposures of metal spray painters to paint mists, lead and chromium have been measured by the US National Institute for Occupational Safety and Health in a variety of industries. The results are summarized in Table 19. High concentrations of paint mist have been recorded in several operations, often linked with the painting of enclosed spaces and internal cavities, faulty ventilation and work practices. Substantial but short-term lead exposure was encountered in situations where lead-based pigments were used, such as for painting transportation and heavy equipment. Elevated but brief exposures to chromium were noted during the spraying of aircraft with primer. No antimony, arsenic, cadmium or mercury was encountered in these studies. Very low levels of tin (2–7 µg/m³) were recorded during the spray painting of dibutyltin dilaurate containing enamel on light aircraft (O'Brien & Hurley, 1981).

In a large study of Swedish car refinishing workshops, averages of 7 mg/m³ mist, 100 µg/m³ lead and 26 µg/m³ chromium were measured during spraying activities; during grinding activities, the corresponding values were 3 mg/m³, 20 µg/m³ and 6 µg/m³. The conditions

Table 19. Painters' exposure (personal breathing-zone samples) to paint mists, lead and chromium in various metal spray-painting operations^a

Operation	Sampling conditions	No. of samples	Exposure level ^b		
			Paint mist (mg/m ³)	Lead (µg/m ³)	Total (µg/m ³)
Light aircraft finishing, primer spraying	25-41 min	3	23.3 ± 1.6	ND	1600 ± 1.6
Light aircraft finishing, topcoat spraying	27-62 min	6	23.3 ± 1.7	ND	-
Light aircraft finishing, stripping operations	19-35 min	6	14.1 ± 2.0	ND-5000	-
Car refinishing	15-45 min	7	8.7 ± 1.6	52 ± 1.5	-
Car refinishing	8 h	7	5.0	30	-
Railroad car	15-60 min	13	43.3 ± 1.4	211 ± 1.7	220 ± 2.2
Heavy equipment	60 min	3	2.0-36.5	230-1300	31-230
Metal furniture	8 h	6 painters	3.7-27.6	ND-1050 ^c	-
Metal furniture, high-solids paints	8 h	6 painters	0.5-6.2	5-26	5-9
Small appliance parts, powder coating, electrostatic spraying	8 h	3	1.3 ± 1.1	-	-
Appliance finishing	8 h	4 painters	21.7-54.5	<6-20	-

^aFrom O'Brien & Hurley (1981)^bGeometric means ± geometric standard deviation, unless otherwise indicated^cOnly 2.5-h samples taken one afternoon showed detectable levels (30-1050)

were thought to be representative of those in the 1960s and 1970s. Simulation of work conditions in 1955 showed low concentrations of lead during the use of all colours except red, when the Swedish exposure limit was exceeded by 70-fold. The actual exposure of painters was believed to be reduced by the use of individual protective equipment (Elofsson *et al.*, 1980). Breathing-zone samples were taken during short-term spray painting operations in a small auto-body repair workshop in the USA. Only one of eight samples, corresponding to a red paint formula, contained significant levels of chromium (490 µg/m³) and lead (210 µg/m³); in all other measurements, the levels of chromium, lead and cadmium were below the detection limit. The concentration of total dust collected during the sanding or grinding of plastic body filler was 5-40 mg/m³ and that of respirable dust, 0.3-1.2 mg/m³ (Jayjock & Levin, 1984). In a factory producing dump-truck bodies and earth-moving machinery in the UK, full-shift personal exposure levels to total paint solids (two samples) were measured as 11.6 and 15.9 mg/m³. After ventilation was properly adjusted, these levels dropped to 1.4 and 5.2 mg/m³. The major pigments used were titanium dioxide and iron oxide (Bradley & Bods-

worth, 1983). At a US plant where truck bodies and refuse handling equipment were made, breathing zone concentrations of solid contaminants measured during various spray painting operations (seven samples varying from 1 to 3 h) were 4.8–47 mg/m³ for total particulates, 20–3000 µg/m³ lead and 10–400 µg/m³ chromium (Vandervort & Cromer, 1975). Low overall exposure levels were found for Swedish spray painters working in a plant manufacturing fire-places, with a total dust level of 1.7 mg/m³, chromium oxide, 5–8 µg/m³ and zinc oxide, 20–30 µg/m³ (Hellquist *et al.*, 1983).

At a US plant where school and general purpose buses were manufactured, employees working in and around the paint booth were reported to be exposed to hexavalent chromium and lead. The concentrations of hexavalent chromium in five personal air samples were 0.03–0.45 mg/m³, with a mean of 0.23 mg/m³; airborne lead concentrations (eight personal samples) ranged from below the laboratory limit of detection (3 µg/filter) to 2.01 mg/m³, with a mean of 0.78 mg/m³ (Zey & Aw, 1984).

A US manufacturer of large-scale weapon, electronic and aero-mechanical systems reported exposure of workers to hexavalent chromium while spraying aircraft wheels with yellow lacquer primers containing zinc chromate. In 12 personal breathing zone samples, the level of chromium[VI] ranged from 13.3 to 2900 µg/m³ with a mean of 606.7 µg/m³ (Kaminsky *et al.*, 1978).

In a US plant in which bridge girders were sprayed with lead silico-chromate paint, personal air levels of lead and chromium (as Cr) in five samples were 0.01–0.25 mg/m³ (mean, 0.08) and 0.01–0.04 mg/m³ (mean, 0.02), respectively (Rosensteel, 1974). Substantial exposure to airborne lead was demonstrated for US workers involved in scraping old lead-based paint from the metallic structure of a bridge and priming it (24–1017 µg/m³); recoating with lead-based paint implied lower exposure levels (6–30 µg/m³). Blood lead levels in these workers were 30–96 µg/100 ml, with 58% above 60 µg/100 ml (Landrigan *et al.*, 1982). In the Netherlands, workers involved in flame-torch cutting of a steel structure coated with lead-based paints were shown to be exposed to 2–38 mg/m³ airborne lead (Spee & Zwennis, 1987).

Blood lead levels have also been measured in workers in various occupations in three Finnish shipyards. Painters were among the most heavily exposed: mean blood levels in a total of 77 painters in the three shipyards were 20–28 µg/100 ml (Töla & Karskela, 1976).

(iii) Other exposures

Use of polyurethane type paints can result in exposure to diisocyanate monomers and their oligomers. In Sweden, 43 car repair painters were exposed to a TWA of 115 µg/m³ hexamethylene diisocyanate (HDI)-biuret oligomer, with a range of 10–385 µg/m³. Very high exposure peaks (up to 13 500 µg/m³) were measured. The concentration of HDI was 1.0 µg/m³ (Alexandersson *et al.*, 1987). In Finland, average HDI and HDI-biuret oligomer levels in four car paint shops during spray painting (ten 5–10-min personal samples, outside respirator) were 49 (± 22 SD) and 1440 (± 1130) µg/m³, respectively. The proper use of a respirator with combined charcoal and particle filters was shown to reduce exposure levels to below detection limits (Rosenberg & Tuomi, 1984). In a US car repainting shop, three short-term air samples (5–13 min) taken in the breathing zone during spray painting operations showed HDI levels of < 130 µg/m³. Similar measurements taken during various light air-

craft finishing operations (7–21 min, eight samples) indicated HDI levels below approximately $70 \mu\text{g}/\text{m}^3$, except for one operation with a level of $250 \mu\text{g}/\text{m}^3$ (O'Brien & Hurley, 1981).

Ambient levels of HDI during the spray application of an enamel top coat at a US airline maintenance facility were <0.04 – $3.20 \text{ mg}/\text{m}^3$, with a mean of $1.1 \text{ mg}/\text{m}^3$ (Okawa & Keith, 1977).

Epoxy paints are usually applied as reactive mixtures of epoxy resins and curing agents, leading to potential exposure to compounds containing the epoxide group. Total epoxide concentrations have been measured in area samples of aerosols collected during three painting operations involving the use of a bisphenol-A diglycidyl ether type of epoxy resin. In a facility producing military aircraft, the use of an epoxy primer did not result in detectable epoxide levels, and the authors surmised that the epoxy-amine curing reaction had probably consumed most of the epoxide group. Epoxide levels of 2 – $12 \mu\text{Eq}/\text{m}^3$ epoxide functional group were recorded during the painting of a tank with coal-tar epoxy coatings and the painting of a metal ceiling using an epoxy architectural coating (Herrick *et al.*, 1988). In a US company that finished structural steel members and other fabricated steel products, the products are blasted with steel shot or sand and spray-painted with two-component epoxy paints or oil-based paints. Personal air levels of epichlorohydrin were reported to range from 2.4 to $138.9 \text{ mg}/\text{m}^3$, with a mean TWA of $64.9 \text{ mg}/\text{m}^3$. Bisphenol A glycidyl ethers were also detected in the workers' breathing zone at levels which ranged from below the limit of detection ($0.6 \mu\text{g}$) to $28.6 \mu\text{g}/\text{m}^3$, with a mean of $9.8 \mu\text{g}/\text{m}^3$ (Chrostek & Levine, 1981).

The major thermal degradation components of epoxy powder paints were identified as phenol, cresols, bisphenol-A, pyridine, 2,3-dimethylpyrazine and formaldehyde; bisphenol-A glycidyl ether was not observed. Levels in the work environment of painters were not measured (Peltonen, 1986; Peltonen *et al.*, 1986). Diethylene triamine, which is a component of curing agents of epoxy paints, was measured in three samples collected from the breathing zone of a painter during spray painting of paper machine cylinders and pulp tanks at a concentration of 0.02 – $0.07 \text{ mg}/\text{m}^3$ (Bäck & Saarinen, 1986).

Operators working in eight plants where coal-tar enamel protective coating was applied to pipelines with heat were exposed to high levels of coal-tar pitch volatiles (see IARC, 1985b) at up to $24 \text{ mg}/\text{m}^3$ of benzene-soluble matter (full-shift samples). The overall respirable concentration of benzo[a]pyrene in the plants averaged $133 \mu\text{g}/\text{m}^3$ (Larson, 1978).

PFE ORIGINAL



NIOSH

Recommendations for Control of Occupational Safety and Health Hazards . . .

Manufacture of Paint and Allied Coating Products

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Cover photograph: This mural representing the paint and allied coating products industry, one of of fourteen murals depicting industrial scenes, is now on permanent display at the Greater Cincinnati International Airport. The murals, designed by Winold Reiss in the early 1930's, originally adorned the walls of Cincinnati's Union Terminal Railway Station.

TABLE II-3. JOB CLASSIFICATIONS IN THE
MANUFACTURE OF VARNISHES

Paint
Ingredients for
R & H

Classification	Description
Reactor operators	Load reactors with raw materials. Adjust and maintain reaction conditions.
Varnish cookers	Cook varnish and maintain reaction conditions (applies only to open-kettle process).
Filter press operators	Filter and reduce the varnish and clean the presses.
Fillers	Fill varnish containers.
Laboratory personnel	Test raw materials. Responsible for finished product testing and for research and development.
Others	Includes packagers, maintenance personnel, shippers, and loading personnel in the warehouse.

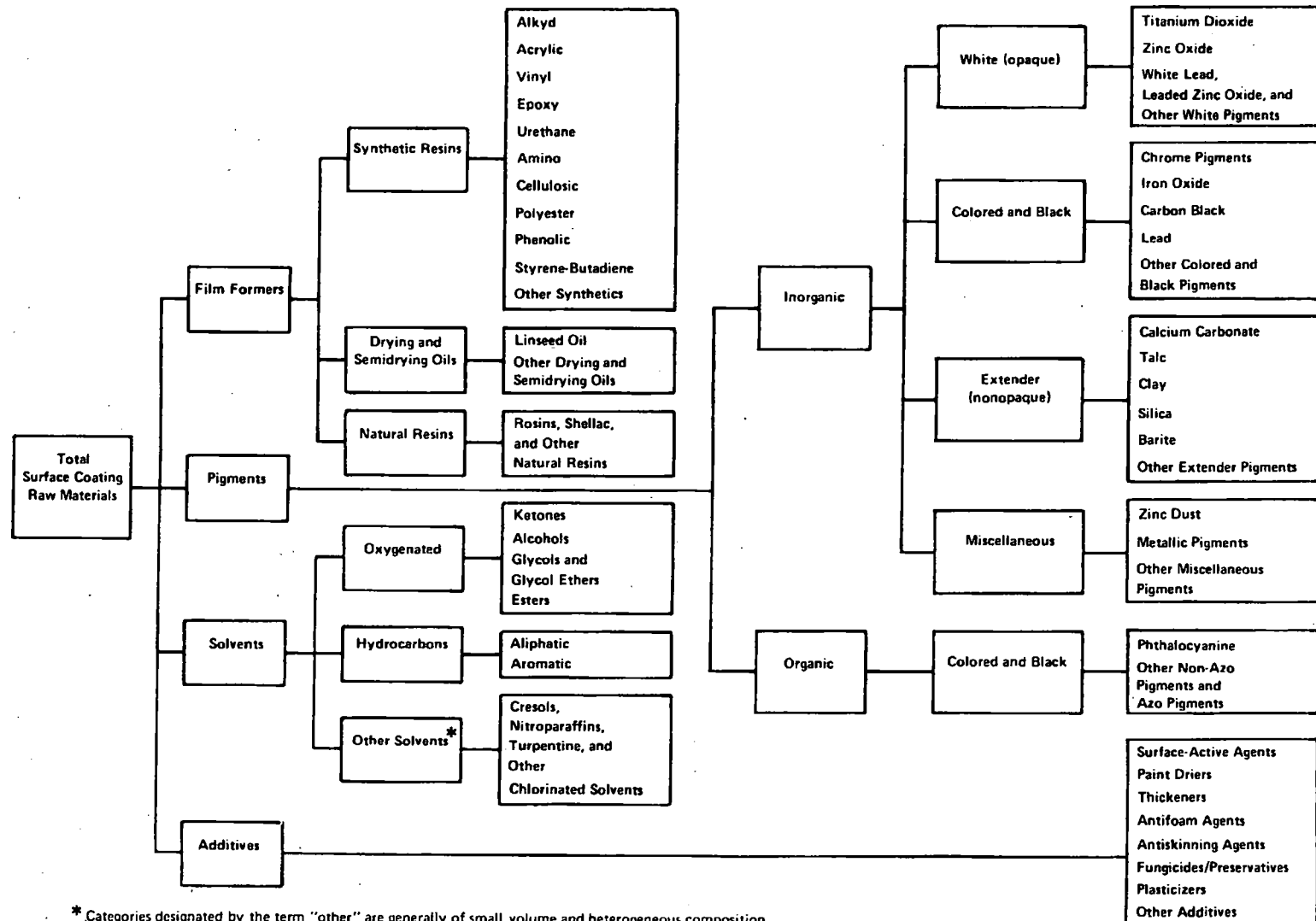
Adapted from Discher et al. [12]

B. Raw Materials

Liquid paint is a suspension of pigment particles in a mixture of film-former and volatile solvent. The solvent, which reduces viscosity to allow easy application, and the film-former hold the pigment in the dried film and cause it to adhere to the coated surface. The pigment confers hiding and coloring power as well as durability to the dried film. Various additives are used to obtain particular characteristics. Although drying is usually accomplished through evaporation of the solvent, drying may also be by polymerization of the film-former through oxidation (e.g., with oils and alkyds), by coalescence (e.g., with latexes), or by chemical reactivity (e.g., with epoxy resins) [13].

In 1980, an estimated 9.5 billion pounds of raw materials (excluding water) were used in the manufacture of paint and allied coating products [6]. The four general categories of raw materials used (film-formers, pigments, solvents, and additives) are identified in Figure II-2.

FIGURE II-2. RAW MATERIALS USED IN THE MANUFACTURE OF COATINGS
(Adapted from Chemical Economics Handbook [1])



1. Film-Formers

Film-formers are the nonvolatile binders or vehicle portions of coatings. They may be classified as one of three different chemical types: synthetic resins, drying and semidrying oils, and natural resins. Synthetic resins account for over 94% of all film-formers and include alkyds, acrylics, vinyls, epoxies, urethanes, amines, cellulose, polyesters, phenolics, styrene-butadienes, and others [1]. Linseed oil is the primary drying oil utilized as a film-former. Natural resin film-formers constituted less than 1% of all film-formers consumed in 1977, in contrast to about 50% prior to World War II [1]. Some of these natural resins include rosins and shellac.

2. Pigments

Pigments are incorporated into coatings to impart color, opacity, and properties such as durability, corrosion inhibition, and mildew control or to be a filler or extender [1]. They are finely powdered solids that are essentially insoluble in the medium in which they are dispersed. Almost all of the pigments utilized in the U.S. (99%) are inorganic [1,6] with titanium dioxide accounting for about one-third of total pigments used [6]. Pigments are generally classified as white (opaque) pigments, colored and black pigments, extenders (non-opaque), and miscellaneous (mainly metallic powders).

Extenders are white pigments that have a low refractive index and have little hiding or coloring ability by themselves in solvent-based coatings but have a strong influence on costs and the performance of most pigmented coatings in which they are used. Extender pigments are used to control gloss, texture, suspension, viscosity, and other physical characteristics of coatings [2,14]. In water-based coatings, however, extender pigments contribute to opacity and hiding ability. Extenders include talc, china clay (aluminum silicate), silica, asbestos, diatomaceous earth, calcium silicate, magnesium carbonate, and mica [2,14].

Generally, pigments are available as dry powders that are shipped in bags or in cardboard or fiber drums. Pigments are also shipped as aqueous slurries and pastes or as pellets.

3. Solvents

The primary function of solvents in paints and coatings is to dissolve or suspend film-formers, thereby providing a consistency suitable for application. Solvents also influence the rate of setting, the drying time, the flow properties, and the flammability of coatings [1]. Water-based paints consist of a dispersion of film-formers within an aqueous medium. Generally, organic solvents are classified as hydrocarbon solvents, oxygenated solvents, and "other." The latter category includes furans, nitroparaffins, chlorinated solvents, and terpenes.

a. Hydrocarbon Solvents

Among the organic solvents, hydrocarbon solvents rank first by volume of use (56%) in paint and allied coatings [1]. They are less expensive than many other types of organic solvents and have many uses. An organic solvent-based coating material that contains no hydrocarbon solvent is unusual. Hydrocarbon solvents used in the paint industry are classified as either aliphatic naphthas or aromatics. Aliphatic naphtha solvents such as mineral spirits or Varnish Makers' and Painters' (VM&P) naphtha are predominantly paraffins, with a smaller but appreciable content of cycloparaffins (naphthenes such as cyclopentane and cyclohexane). These solvents may also contain as much as 20-30% aromatics [2]. Mineral spirits constitute about three-fourths of all hydrocarbon solvents used in the paint and allied coating products industry overall. The aromatic hydrocarbon solvents such as toluene, xylene, high flash solvent naphthas, and aromatic naphthas predominantly exhibit higher solvency than aliphatic solvents.

b. Oxygenated Solvents

Oxygenated solvents are so designated because of the presence of oxygen which contributes polarity (a difference in the electric charge on various portions of the materials). This polarity is the fundamental difference between oxygenated and hydrocarbon solvents, which are essentially nonpolar. Because of their polarity, many oxygenated solvents are water-soluble and are better solvents for the more polar film-formers such as shellac, cellulose esters, amino-formaldehydes, vinyls, acrylics, epoxies, polyurethanes, and silicones [15]. Oxygenated solvents account for about 42% of the organic solvents used in the paint and allied coatings industry [1] and include glycols, glycol ethers, glycol ether esters, water-miscible alcohols such as methanol, ethanol, butanol, and isopropanol, acetate esters, and ketones such as acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) [6]. Since they are more expensive than the hydrocarbon solvents, a mixture of oxygenated and hydrocarbon solvents is used in most paint formulations [15].

c. "Other Solvents"

Other solvents, which account for only 1% of the organic solvents used, include furans such as tetrahydrofuran and tetrahydrofurfural alcohol, nitroparaffins such as 2-nitropropane, chlorinated solvents such as methylene chloride, and terpenes such as turpentine, dipentene, and pine oil [2,15].

4. Additives

Many substances that contribute to the ease of manufacture, the stability of the paint in the package, the ease of application, or the quality or appearance of the applied film are used in relatively small quantities in paint formulations. These substances are referred to under the broad term "additives." Each additive rarely exceeds 1% of the total formulation, and the total amount of all additives seldom exceeds 5% of the paint product [16]. The major classes of additives are plasticizers, surface-active agents, flow modifiers, driers, anti-skinning agents, biocides, and "other."

a. Plasticizers

A plasticizer is a substance added to a coating material to keep the finished film flexible and to avoid undesirable effects such as cracking or checking, without appreciable sacrifice of such desirable effects as film strength, continuity, and resistance to attack by chemicals [17]. True plasticizers are permanent and relatively nonvolatile components of coating films. Plasticizers account for about one-third of the additives consumed in coatings [1]. Over 500 different plasticizers are available [2].

b. Surface-Active Agents

Surface-active agents or "surfactants" are added to aqueous coatings (such as latexes) and comprise over 20% of the additives used in paints [1]. There are four general groups: anionic surfactants, used primarily to promote pigment dispersion by providing better wetting of the particles; nonionic surfactants, used to stabilize total dispersed systems; antifoam agents, used to prevent, reduce, or eliminate foam formation during coatings manufacture and application; and emulsifiers, which are materials used to stabilize mixtures of immiscible liquids such as oil and water by reducing interfacial tensions between liquids [16,17].

c. Flow Modifiers

Flow modifiers such as thickening (bodying) agents affect the viscosity of coatings. Thickening agents are used to provide desired paint consistency, prevent pigment settling, and assist in applying films of adequate and uniform thickness [16].

d. Driers

Driers promote or accelerate the drying, curing, or hardening of oxidizable coatings [16]. Driers should be clearly differentiated from curing agents that chemically react or condense with the coating material to become an integral part of the final polymer composition [16].

e. Anti-skinning Agents

Skinning refers to the drying of a coating, but at the wrong time and in the wrong place (e.g., while it is still packaged). Oxidative polymerization of the film-formers at the air-liquid interface can lead to the formation of a solid or gelatinous skin on the surface. Anti-skinning agents are volatile antioxidants which prevent oxidation of the paint in the package and volatilize while the coating is drying.

f. Biocides

Fungicides and preservatives are used to control the growth of fungi and other microorganisms. Microorganisms cause spoilage or deterioration and premature failure of paint and other coatings. Bacteria and fungi can use coatings, particularly water-based coatings, as food sources [2,16]. Biocides are used as mildewcides in exterior house paints, as antifoulants in marine paints, as preservatives and stains for wood used primarily as furniture, and as in-can preservatives in latex architectural coatings [9]. Zinc oxide, which is also a white pigment, is commonly used to confer mildew resistance to paints [13].

Due to environmental concerns, the use of phenylmercury salts as a biocide is declining [9]. Other traditional biocides such as creosote, pentachlorophenol, and coal tar products which are used in wood stains, preservatives, and coatings are also coming under regulatory scrutiny [9]. Replacements for these biocides include copper naphthenate, tributyltin oxide, zinc naphthenate, N-(trichloromethylthio)phthalimide, and cuprous oxide [9].

g. "Other" Additives

Many other substances are added to coatings in small amounts. These include coalescing agents, wet edge extenders, freeze-thaw and heat stabilizers, odorants, flame retardants, anti-livering agents, ultraviolet (UV) light absorbers, and agents that promote mar resistance [1].

C. Manufacturing and Related Operations

The manufacture of paint and allied coating products involves the assembling of materials, mixing, dispersing, thinning and adjusting, filling, and warehousing. Other related activities include materials handling, laboratory work, and shipping. The flow of materials in a typical paint manufacturing plant is shown in Figure II-3.

The manufacture of paint and allied coating products is essentially a series of unit operations (physical procedures) involving little or no chemical

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**GUIDES TO POLLUTION PREVENTION:
The Paint Manufacturing Industry**

**RISK REDUCTION ENGINEERING LABORATORY
AND
CENTER FOR ENVIRONMENTAL RESEARCH INFORMATION
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268**

NOTICE

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Worksheets are provided for conducting waste minimization assessments of paint manufacturing facilities. Users are encouraged to duplicate portions of this publication as needed to implement a waste minimization program.

SECTION 2

PAINT MANUFACTURING INDUSTRY PROFILE

Industry Description

As defined by Standard Industrial Classification (SIC) 2851, the paints and allied products industry "comprises establishments primarily engaged in the manufacture of paints (in paste and ready mixed form), varnishes, lacquers, enamels and shellacs, putties, wood fillers and sealers, paint and varnish removers, paint brush cleaners, and allied paint products." Establishments engaged in the manufacture of pigments (organic or inorganic), resins, printing inks, adhesives and sealants, or artist materials are not included.

The industry is comprised of roughly 1,375 establishments nationwide. Approximately 44 percent of all paint manufacturing plant sites are located in five states (California, New Jersey, New York, Illinois, and Ohio), with 67 percent being located in ten states. Most of the plants are located near major population centers.

Products and Their Uses

Most small plants produce paint in 10 to 500 gallon batches. Plants with more than 20 employees produce paint in 200 to 3,000 gallon batches. Overall, the paint industry sold 8.6 billion dollars worth of product in 1983 (\$3.9 billion for architectural coatings, \$3.0 billion for product coatings, and \$1.7 billion for special purpose coatings) (Webber 1984). The amounts and distribution of products manufactured by the paint industry in 1983 are shown in Table 1.

For an average paint plant located in the U.S., 60 percent of its total annual production would be solvent-based paint, 35 percent would be water-based paint, and 5 percent would be allied products. While a large percentage of paint used for architectural coating is water-based (more than 70 percent), solvent-based paint is still predominantly used for product and special purpose coatings.

Table 1. 1983 Paint Products and Use Distribution

Architectural Coatings	463 million gallons
Product Coatings	331 million gallons
Metal containers	19%
Automotive	16%
Machinery	6%
Sheet, strip and coil	6%
Metal furniture	5%
Other	48%
Special Purpose Coatings	130 million gallons
High performance maintenance	31%
Automotive and machinery refinishing	29%
Traffic paint	14%
Other	26%

Source: Chemical and Engineering News (Webber 1984).

Raw Materials

Annual consumption rates of raw materials used by the paint manufacturing industry are shown for 1982 in Table 2.

The major raw materials used to manufacture paint are resins, solvents, drying oils, pigments, and extenders. Based on the wide variety of paints produced, no one type of material dominates the market.

Process Description

Detailed process flow diagrams of paint manufacturing have been presented in the open literature (Haines 1954, Payne 1961). The following description briefly highlights the production of the industry's two main products: solvent-based paint and water-based paint. At a typical plant, both types of paint are produced. A block flow diagram of the steps involved in manufacturing paint is presented in Figure 2.

Table 2. Raw Materials Used by the Paint Manufacturing Industry in 1982

Materials	Usage
Resins	1844 million lbs/yr.
Alkyd	33%
Acrylic	19%
Vinyl	19%
Other	29%
Solvents	3774 million lbs/yr.
Aromatic	30%
Aliphatic	27%
Ketones	17%
Alcohols	12%
Other	14%
Pigments	1062 million lbs/yr.
Titanium dioxide	65%
Inorganic(a)	33%
Organic	2%
Extenders	1162 million lbs/yr.
Calcium carbonate	31%
Talc	25%
Clay	23%
Other	21%
Miscellaneous	220 million lbs/yr.
Drying oils	41%
Plasticizers	18%
Other	41%

Source: Chemical Economics Handbook (SRI 1981) data for 1977 adjusted for 1982 production rates.

- (a) Approximately 60 percent of the inorganic pigments used consisted of iron oxide, zinc oxide, zinc dust, and aluminum paste; 27 percent consisted of lead and chrome compounds; and 13 percent consisted of other compounds.

The production of solvent-based paint begins by mixing some of these: resins, dry pigment, and pigment extenders, in a high speed mixer. During this operation, solvents and plasticizers are also added. Following the mixing operation, the batch frequently is transferred to a mill for additional grinding and mixing. The type of mill is dependent on the types of pigments being handled, so that no one style is universal. Next, the paint base or concentrate is transferred to an agitated tank where tints and thinner (usually a volatile naphtha or blend of solvents) and the balance of the resin are added. Upon reaching the proper consistency, the paint is filtered to remove any non-dispersed pigment and transferred to a loading hopper. From the hopper, the paint is poured into cans, labeled, packed, and moved to storage.

The water-based paint process is very similar to the solvent-based process. The major difference is the substitution of water for solvent and the sequencing of material additions. Preparation of water-based paint begins by mixing together water, ammonia, and a dispersant in a mixer. To this mixture, dry pigment and pigment exten-

ders are added. After mixing, the material is ground in a mill and then transferred to an agitated mix tank. Four additions of materials occur in this tank. First, resin and plasticizers are added to the mixture; second, a preservative and an antifoaming agent are added; third, a polyvinyl acetate emulsion is added; and fourth, water is added as a thinner. Following this mixing operation, the handling of the paint is similar to that for solvent-based paints. At many facilities the grinding and the mixing and grinding operation may be bypassed with all the dispersion operations occurring in a single high-speed mixer.

Waste Description

Typically, paint facilities segregate and store waste only to the degree required by the waste disposal contractor. Since the degree of segregation can affect the amount of material having to be classified as hazardous, and the cost of disposing of hazardous material is increasing, paint facilities are taking a more active role in waste management. The major wastes that the paint industry must manage are empty raw material packages, dust from air pollution control equipment, off-specification paint, spills,

PLANT A WASTE MINIMIZATION ASSESSMENT

Planning and Organization

Planning and organization of the assessment was done by the consulting firm with the assistance of personnel from the paint manufacturing firm. Initial contact was made with the paint manufacturer's plant operations manager, a high level manager who could provide the company's commitment to cooperate in the assessment and provide all the necessary facility and process information. The goal of this joint effort was to conduct a comprehensive waste minimization assessment for the plant. Under different circumstances, in a company with its own ongoing waste minimization program, goals could be set to target a specific amount or type of waste to be reduced; or to conduct a waste minimization assessment each year; or other goal. The waste assessment task force in the case of Plant A consisted of the consultants working together with the plant manager. This task force also functioned as the assessment team.

Assessment Phase: Process and Facility Data

Initial discussions by telephone between the consultants and the plant manager were used to request process and facility information prior to a site visit. These discussions also served to identify particular waste streams of concern to plant managers -- in particular, the disposal of cartridge filters.

At the site visit, the plant operations manager and consultants met to review the facility's operations and its potential target waste streams. The manager conducted a facility tour and introduced the consultants to process managers and workers involved in materials and waste handling. Some of these people were interviewed to obtain information about specific procedures used at the plant.

FACILITY DESCRIPTION

Plant A produces a wide variety of architectural coatings: 76 lines of paint products and eight lines of aerosol spray paints for distribution through retail outlets, and 55 lines of aerosol and specialty paints for sale through

distributors. About 80 percent of the paints produced at this facility are water-based and the remainder are solvent-based. The water-based coatings are latexes and the solvent-based coatings are mostly alkyd resins dissolved in solvents. Figure A-1 presents the annual production rates of paints since 1982. Most of the paints produced are for use by the general public.

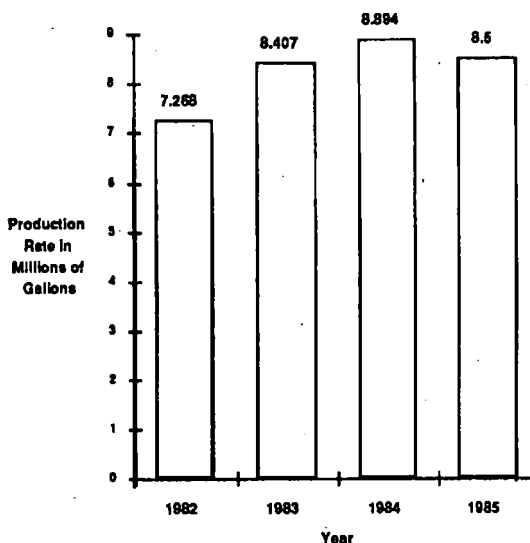


Fig. A-1. Annual Production Rates of Paints at Plant A since 1982

RAW MATERIALS MANAGEMENT

The raw materials used at Plant A include resin solutions, emulsions, solvents, pigments, bactericides, fungicides, and extenders. Some defoamers and surfactants are also added to the water-based batches. Table A-1 lists the principal raw materials used by the plant in 1985.

The solvents used at this facility include aliphatics, aromatics, ketones, or glycol ethers. Glycols such as diethylene glycol, propylene glycol, or Texanol are added to the water-based formulations to increase the paint drying time and to act as an anti-freeze. The solvents are

either delivered and stored in drums or delivered in bulk and held in the above-ground diked storage tanks.

The pigments are delivered in bags when used in powder form, and in drums or in bulk when used in slurried form. The use of slurried pigments is predominant in water-based formulations. Some solvent-based formulations use pigments in paste form, which are purchased in five gallon containers.

A complete inventory check is done four times a year, though limited inventory checks are done on a daily basis. Plant A is planning to convert from a manual to a computerized inventory system.

Table A-1. Raw Materials Used at Plant A

Description	Material
Solvents	Aliphatics
	Aromatics
	Ketones
	Alcohols
	Diethylene glycol
	Propylene glycol
Resins	Acrylics
	Vinyl-acrylics
	Alkyds
Pigments	Titanium dioxide
	Organic pigments
	Red oxide
	Yellow oxide
	Other inorganic pigments
Extenders	Calcium carbonate
	Clay
	Talc
	Silicates
Miscellaneous Additives	Bactericides and fungicides
	Surfactants and defoamers
	Viscosity modifiers
	Ammonia
	Others

PROCESS DESCRIPTION

The production of paints at Plant A is shown in block flow diagrams in Figures A-2 through A-7. The description is general enough to apply to the production of both solvent- and water-based paints in most cases.

The first step in paint production is the dispersion of the pigments (see Figure A-2). The pigments in emulsion

or slurry form, along with the solvents, resins, and additives are added directly to a mill in the primary dispersion step. The dispersed material from the mill is then pumped directly to the let-down tanks. In less than five percent of the cases, the pigments (in emulsion, slurry, or dry form) are added to other raw materials in a portable tank or a small container. The contents of the tank or container are then dispersed in a sand mill, ball mill, or high-speed mill and either collected in another portable tank or directly added to the let-down tank. In all cases, the portable tanks or containers are reused several times without any cleaning but are ultimately sent for cleaning.

The dispersion mills are dedicated to a particular type of product to the fullest extent possible. The dedicated mills are not cleaned. The non-dedicated mills are purged with solvent or water at the end of the dispersion process and the wash material is mixed with the dispersed product in the let-down step.

In the let-down step (see Figures A-4 and A-5), the dispersed pigments from milling operation are mixed in portable or stationary tanks with additional diluents, resins, and additives. The tanks have capacity varying from 50 to 10,000 gallons. The additives constitute bactericides, fungicides, surfactants, defoamers, or extenders. The bactericides and fungicides used for water-based batches are mercury-based whereas non-mercurials are used for solvent-based batches. Solvents such as diethylene glycol or propylene glycol are added to water-based paints to extend the drying time and act as an anti-freeze in cold climates.

The stationary tanks have a capacity greater than 400 gallons while the portable tanks have a 50- to 400-gallon capacity. About 25 percent of the total number of batches are let down using portable tanks, which accounts for less than 10 percent of the total paint volume produced at Plant A. The mixing in the tanks is performed using turbine mixers. When the properties of the batch reach therequired standards, the mixing is stopped. The tank contents are then pumped through bag filters to the filling unit, which can fill five gallon, one gallon, 1/4 gallon, or 1/2 pint cans.

WASTE DESCRIPTION

The principal waste streams generated by Plant A include the following:

- Equipment cleaning wastes
- Obsolete stock

PLANT B WASTE MINIMIZATION ASSESSMENT

The waste minimization assessment of Plant B followed the same protocol used for Plant A, and included:

- Planning and organization
- Assessment phase
- Feasibility analysis phase

Implementation of selected waste minimization options was left to the discretion of Plant B.

Planning and Organization

Planning and organization of the assessment were a joint effort of the consulting firm and the paint manufacturing plant's operations manager. As summarized in Figure 1, this phase of the assessment involved getting company management commitment to the project, setting goals for the assessment, and establishing a task force (the consultants working in cooperation with the plant operations manager) to conduct the assessment.

Assessment Phase: Process and Facility Data

The consultants worked with the plant operations manager to establish a data base of the facility's raw material needs, materials handling procedure and operations processes. Block flow diagrams were drawn up to identify where materials are used and where waste is generated. Initial study of this information and discussions of waste stream concerns at the plant served as preliminary steps to the site inspection, during which additional process and waste handling information was obtained.

FACILITY DESCRIPTION

Plant B produces a wide variety of industrial coatings. About 90 percent are solvent-based; the remainder are water-based. About 10 years ago, the water-based paints constituted only 1 percent of total production.

The solvent-based paints produced include pigmented tints, pigmented non-tints, lacquer thinners, unpigmented paints (clears), and stains. The water-based formulations

are mostly emulsion paints. The production rates of the major products are listed in Table A-5.

Table A-5. Coatings Produced by Plant B in 1985

Product	Production Rate (gal/yr)
Pigmented products (enamels)	360,000
Clear products (lacquers & varnishes)	1,220,000
Reducers & solvents	260,000
Stains & fillers	310,000

RAW MATERIALS MANAGEMENT

Numerous organic solvents are used at Plant B in paint production. Other raw materials in paint production include resins, pigments, extenders, and additives. Table A-6 presents the consumption rates of the major raw materials in 1985.

The selection of solvents used in paint production is based on the end use of the paint. The solvents used at Plant B include methanol, methyl ethyl ketone (MEK), Toluol-6, toluene, lacquer thinner, and mineral spirits. The solvents are purchased in bulk or in drums. The solvents in bulk form are stored in underground storage tanks. The solvents in drums are stored in an outdoor storage area.

The pigments are delivered in plastic or paper bags, which are stored in an indoor storage area. The inventory is typically capable of meeting the production requirement for two months. In addition to raw materials, some process intermediates are also stored indoors.

Each of the raw materials is assigned an identification number for inventory control and product formulation. The amounts of various raw materials for each batch are determined through a computer and the data is punched out on computer-generated batch cards. The employee at the production unit follows the instructions given on the cards and obtains the raw material from the storage area using the coding sequence for the material.

PROCESS DESCRIPTION

The following description highlights the production of a solvent-based paint at Plant B.. The block flow diagram for this process is presented in Figures A-10 through A- 12.

The production of the paint begins with dispersing the pigments in either a roll mill or a sand mill. The sand mills are horizontal or vertical and employ sand/glass/steel bead/shot to disperse the pigments in a small quantity of solvent/resin mixture. The primary dispersion is carried out in batches of 30 or 55 gallons. After passing through the mill, the mixture of pigments and solvent/resin is collected in another container and sent to intermediate storage, let-down, or the next step in production. Sometimes, the mixture is passed through the mill up to 3 times to achieve the required degree of dispersion. In such instances, two containers (feed container and receiver container) are used. The same containers are used for all the passes through the mill, and the containers are cleaned after each pass.

Table A-6. Raw Material Consumption Rates at Plant B in 1985

No.	Material	Annual Consumption Rate
Solvents		
1.	Methanol	48,000 gal.
2.	Methyl ethyl ketone	178,000 gal.
3.	Tolusol-6	361,000 gal.
4.	Solvent IB	186,000 gal.
5.	Lacquer thinner (blend)	170,000 gal.
6.	Mineral spirits	132,000 gal.
7.	Filmcol A-4	82,000 gal.
8.	Isobutyl Isobutyrate	51,000 gal.
Resins		
9.	Beckosol	41,515 gal.
10.	Coconut Alkyd	33,575 gal.
11.	Rhophex WL-91	16,000 gal.
Pigments		
12.	Titanium dioxide	350,000 lbs.
13.	Yellow oxide	32,000 lbs.
14.	Burnt umber	51,000 lbs.
15.	Van dyke brown	56,000 lbs.
Extenders		
16.	Calcium carbonate	52,000 lbs.
17.	Talc	128,000 lbs.
18.	Clay	30,000 lbs.
Miscellaneous		
19.	Drying oils	30,000 gal.
20.	Plasticizers	10,000 gal.

The let-down step consists of filling the mixing tank with the primary dispersions, solvents, plasticizers and other additives. The solvents are pumped into the tanks using the filling system shown in Figure A-13. The contents are then mixed. For portable tanks, high-shear vari-speed mixers are employed. For the stationary tanks a low-speed mixing is used. When the tank contents attain the proper viscosity, color, and gloss, the mixing is stopped and the contents are filtered and dispensed into product containers. The filtration is achieved using bags, cartridge filters, or vibrating screens. If the tanks are portable, they are moved to the filling area and the contents are gravity fed to the filling unit.

The batch sizes are 55, 110, 220, 300 or 550 gallons for the portable tanks. Larger batches are prepared in stationary tanks with a capacity of 1000, 1500, or 3000 gallons. Figure A-13 shows the layout of the tanks in the production area. The stationary tanks are usually dedicated to one product and therefore, no cleaning is required between subsequent batches. At present, the products prepared in the stationary tanks (in order of decreasing production quantity) are clears, stains, and enamels. Similarly, the major products produced using portable tanks are stains, enamels, and clears.

WASTE DESCRIPTION

The major wastes generated by Plant B are (in order of decreasing volume): equipment cleaning waste, obsolete products, returns from customers, off-specification products, spills, filter bags and cartridges, and empty bags and packages. The sections below discuss each of these wastes.

The solvent waste is sent to an off-site recycler for reclamation. On-site solvent recovery was conducted in the past, but was discontinued when it proved too expensive. The off-site recycler charges \$0.65/gal of spent solvent to reclaim it at 60 % minimum yield and return it to Plant B. The distillation residues generated during the reclamation are disposed of at a surcharge of \$0.75/gal-spent solvent. The off-site recycler charges \$1/gal if the solvent waste is incinerated in a cement kiln. The off-site recycler is planning to substantially increase its service charges (e.g. \$ 2.60/gal for incineration) in the near future.

Table A-7 presents the costs (\$/ton) of some solvents used by Plant B. Also presented are some disposal cost figures from an off-site recycler.

Sherwin-Williams/Hilliards Creek

New Jersey

EPA ID#: NJD980417976

EPA REGION 2

Congressional District(s): 01

Camden
Gibbsboro

NPL LISTING HISTORY

Proposed Date: 4/19/2006

Final Date: 3/19/2008

Site Description

The Sherwin-Williams/Hilliards Creek site is located in Gibbsboro, Camden County, New Jersey. The Sherwin-Williams/Hilliards Creek site includes, but is not limited to, contaminated soil and ground water on the former Lucas Paint Works Plant (Lucas plant) and contaminated soil, sediment, and surface water associated with Hilliards Creek. The former Lucas plant encompassed 60 acres of land and was bounded to the north by Silver Lake and Route 561, to the east by United States (US) Avenue, to the south by vacant land, a cemetery, and Bridgewood Lake, and to the west by Clementon-Gibbsboro Road. Hilliards Creek, also known as Millard Creek, flows southwesterly through the former Lucas plant, under Foster Avenue, then turns west under W. Clementon Road, receives the outflow of Bridgewood Lake, and continues west to Kirkwood Lake. Approximately 1,000 feet upstream from Kirkwood Lake, Hilliards Creek receives surface water flow from Nichols Creek. It merges with the Cooper River just before it enters Kirkwood Lake. Kirkwood Lake and portions of Hilliards Creek are located in Voorhees and Lindenwold Townships, Camden County, New Jersey.

The manufacturing history of John Lucas and Company began in 1849, and dry colors were among the first products manufactured. Dry color was the largest operation at the Lucas plant through the end of the 19th century. Chrome yellow and Prussian blue were the two major pigments produced at the Lucas plant. The Lucas plant made the first chrome greens and chrome yellows produced in America. The basic pigments used by the Lucas plant were lead and zinc oxides, white lead, non-lead chrome green, and chrome yellow. White lead was ground at the plant. Later, the Lucas plant produced 24 different varieties of varnish.

When it was owned and operated by the Sherwin-Williams Company, the plant included: an area for unloading raw materials from railroad cars; two tank farms for raw materials including storage tanks constructed prior to 1908; several storage areas for drummed raw materials; an industrial and domestic wastewater treatment and disposal system consisting of unlined percolation/settling lagoons; a solid waste disposal area for paint sludges; an extensive system of pipes to transport raw materials; and a drum cleaning area. Raw materials were mixed and processed in a number of specialized buildings located throughout the plant area. Raw materials stored on the plant included: naphtha (8,000 gallons); xylene (26,000 gallons); mineral spirits (100,000 gallons); toluene and solvent blends (65,000 gallons); as well as aromatic naphtha (1,500 gallons).

In June 1981, a majority of the Sherwin-Williams Company plant was sold to developer Robert K. Scarborough. Scarborough developed the former plant into a light industrial complex named The Paint Works Corporate Center (PWCC). The PWCC is made up of nine buildings. In December 1987, a portion of the former plant property was sold to Brandywine Realty Trust.

Site Responsibility: The site is currently being addressed through Federal action and potentially responsible party (PRP) involvement.

Threat and Contaminants

Former Manufacturing Plant Area: In 1976, New Jersey Department of Environmental Protection (NJDEP) directed Sherwin-Williams to conduct a subsurface investigation in the former lagoon area. According to the remedial investigation (RI) report, a sludge pit was located in the area of the lagoons. The depth of the sludge pit was 20 feet. Sludge was encountered at the base of the lagoons at depths of 2 to 5 feet. Twenty eight soil borings were drilled in the lagoon area to approximate the depth of contamination.

In January 1990, the NJDEP issued a Spill Act Directive to Scarborough (the owner of the Lucas plant property) and the Sherwin-Williams Company requiring that a remedial investigation and feasibility study (RI/FS) be conducted at the former manufacturing plant area and the adjacent lands. The Sherwin-Williams Company subsequently entered into an

Administrative Consent Order (ACO) with NJDEP to conduct the RI/FS. The subsequent RI was conducted at the former manufacturing plant area from August 1991 through January 2000. Groundwater seeps, which contained visible contamination (located on the facility), were identified as an area of Immediate Environmental Concern (IEC). Sherwin-Williams entered into an ACO with NJDEP to address this IEC.

Free-phase product is present in the groundwater at the former manufacturing plant area, near the areas of former Buildings 50, 67, and former Tank Farm A. The free-phase product (non-aqueous phase liquids - NAPL) plume in groundwater near former Buildings 50 and 67 was initially identified in 1983 when an oily substance was observed in the parking lot between former Buildings 50 and 67 (also known as the Academy Paints Building). The oily substance flowed overland to a storm water catch basin in the parking lot then into a storm sewer that ultimately discharged into Hilliards Creek. The product was observed on many occasions during construction of the PWCC that now occupies the former manufacturing plant area. The free-phase product composition includes: benzene, ethylbenzene, xylene, naphthalene, and 2-methylnaphthalene. Analysis of the product indicates that it is paint thinner.

In 1987, contaminated soil was identified in the area of Buildings 50 and 67 during a subsurface soil investigation. The source of the contaminated soil is the free-phase product. Soil samples were analyzed for priority pollutants and total petroleum hydrocarbons, revealing the presence of petroleum hydrocarbons, VOCs (xylene), SVOCs [pentachlorophenol, di-n-butyl phthalate, bis(2-ethylhexyl)phthalate], cyanide, chromium, copper, and lead.

Numerous monitoring wells were installed throughout the former manufacturing plant area by the Sherwin-Williams Company. Data collected from these wells has shown the continued presence of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and to a lesser extent inorganic compounds.

Hilliards Creek: On September 30, 1999, the Agency for Toxic Substances and Disease Registry ("ATSDR") concluded that based on available Hilliard Creek data, the Creek currently poses an urgent health hazard to children and adults who utilize the Site and recommended that exposure to individuals who frequent the Site should be eliminated and that further delineation of Site related media should be conducted.

Historic sampling, as well as more recent sampling performed during the 2005, 2006, and 2008 Remedial Investigation (RI) field sampling activities has indicated that inorganic hazardous substances such as arsenic and lead were detected at concentrations significantly above background levels in surface water, soil and sediment sampled from the site. In addition, based on the results of the 2005 and 2006 RI sampling results, EPA requested that RI sampling activities be performed in Kirkwood Lake (approximately 0.8 miles long), which is fed directly from Hilliards Creek. Soil and sediment samples collected from Kirkwood Lake have also exhibited concentrations of lead and arsenic at elevated concentrations.

In 2010 a Supplement Work Plan for all media (soil, sediment, surface water, and groundwater) was implemented at the former Sherwin-Williams paint plant (also referred to as the Former Manufacturing Plant). In addition, investigation into underground anomalies was also performed. The data and field activities were summarized in reports and submitted to EPA and NJDEP; the soil, sediment, surface water and underground anomaly investigation report was submitted in March 2011 and the groundwater report was submitted in June 2011. EPA and NJDEP reviewed the reports and made recommendations for additional investigations. Sherwin-Williams has agreed to perform the additionally requested groundwater investigation sampling, as well as the proposed soil sampling and investigation into additional underground anomalies. EPA anticipates that all necessary sampling should be completed by December 2013.

Cleanup Approach

Immediate Actions: In 1976, NJDEP directed the Sherwin-Williams Company to conduct a subsurface investigation in the former lagoon area. According to the RI report, a sludge pit was located in the area of the lagoons. The depth of the sludge pit was 20 feet. On August 17, 1978, NJDEP issued an AOC to the Sherwin-Williams Company to remove sludge in the area of the lagoons and to monitor ground water. In 1979, a total of 8,096 cubic yards of sludge was removed from the lagoon area. After the sludge was visibly removed, the lagoons were filled with clean fill. The removal was considered complete when all the visually identifiable sludge and contaminated soils were removed. Since the removal action was based on visually removing the waste, it cannot be documented that all the contamination was removed. The contamination associated with the releases to ground water and surface water has not been addressed.

During a 1996 EPA removal action, the Sherwin-Williams Company recovered 13,910 gallons of the mixture of nonhazardous liquid, water, and oil from the free-phase product groundwater plume and disposed the material off the property. After the removal action was completed, residual contamination remained in this area and Hilliards Creek. In November 1997, the installation of the Free Product Recovery (FPR) and Soil Vapor Extraction (SVE) systems were completed east and north of Building 67 and south of Building 50.

On April 9, 2002, free-phase product from the FPR system was observed in the storm water drain north of former Building 67 and in Hilliards Creek. Product was pumped out of the storm water drain, and additional measures were

taken to prevent further releases to the drain and Hilliards Creek.

ENTIRE SITE: On September 30, 1999, EPA issued an AOC to The Sherwin-Williams Company to conduct a Remedial Investigation and Feasibility Study (RI/FS). The objective of the RI/FS is to determine the full nature and extent of contamination and any potential threats to the public health, welfare, or the environment caused by any release or threatened release of hazardous substances, pollutants, or contaminants in connection with the Site; and to determine and evaluate alternatives for the remediation or control of any release or threatened release in connection with the Site. The Sherwin-Williams Company initiated RI field sampling activities in the spring of 2005. RI field sampling operations included the collection of: soil, sediment, surface water and groundwater samples. Additional RI field sampling activities were performed in Hilliards Creek during 2006. In 2007, surface water, sediment and soil sampling operations were performed in Kirkwood Lake (downstream from Hilliards Creek), sampling has revealed that arsenic and lead are present in the soil and sediment. Additional sampling was performed in Kirkwood Lake in 2008 to delineate the vertical extent of sediment contamination.

In the fall of 2010 soil sampling was also performed at several homes adjacent to Hilliards Creek (close to the former paint manufacturing plant). In addition, a comprehensive residential soil sampling program was performed at the homes along Kirkwood Lake. Approximately 30 homes were sampled in the Summer of 2011. Data from all residential soil sampling programs has been shared with the property owners. All data will be assessed during the human health risk assessments and any recommendations for remedial action will follow. No further sampling of these homes is anticipated.

Cleanup Progress

A total of 8,096 cubic yards of sludge was removed from the former lagoon area. After the sludge was visibly removed, the lagoons were filled in with clean fill. The removal was considered complete when all the visually identifiable sludge and contaminated soils were removed.

Sherwin-Williams recovered 13,910 gallons of the mixture of non-hazardous liquid, water, and oil from a free-phase product groundwater plume and disposed of the material off the property. In November 1997, the installation of the FPR and SVE system was completed east and north of former Building 67 and south of former Building 50. As of June 20, 2002, a total of 44,785 gallons of product have been recovered and removed off site for disposal since startup of the system in November 1997. Approximately 8,275 gallons of this total volume collected was primarily product from the product recovery tank. The remaining 36,510 gallons of product were collected during the ground water seep response and recovery efforts associated with the FPR and SVE system.

In addition, a September 1999 Removal AOC with EPA required the Sherwin-Williams Company to install fencing around the former Wildlife Refuge area of Hilliard's Creek. This area once contained a nature-trail which permitted local residents access to areas of the impacted creek (soils, surface water, and sediment). Due to repeated breaches of the security fence, by trespassers, Sherwin-Williams recently installed a video surveillance system that is equipped with motion detection system as well. Through these efforts, EPA has reduced the short-term risks associated with exposure to the inorganic hazardous substances.

Site Repositories

Copies of the RI/FS Work Plan, Field Sampling Plan and Quality Assurance Project Plan can be found at the Gibbsboro Borough Hall/Library at 49 Kirkwood Road, located in Camden County, Gibbsboro, New Jersey; additional copies can be found at the Camden County Public Library, 203 Laurel Road, Voorhees Township, New Jersey.

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- INNOVATION -

REVOLUTIONIZING PAINTS

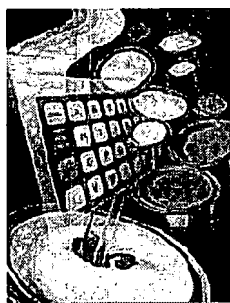
The Birth of Acrylic Latex Paints



Paint is made of three main ingredients: pigment, a binder (or resin), and a liquid (or vehicle). Pigments give paints their color. Binders are the "sticky" solids that hold everything together. And, traditional paint vehicles were oils. Latex paints, introduced after WWII, were the first paints to use water as the liquid. Latex paints dried quicker, were easier to clean up, and weren't flammable like oil-based paints. These

were appealing qualities to the new "do-it-yourself" homeowner in the post-war housing boom of the 1950s.

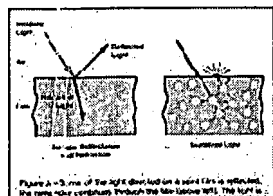
Early latex paints used rubber-based binders. But binders didn't have to be made of rubber, and Rohm and Haas looked for ways to create better binders from acrylics. After much trial and error in cooperation with paint manufacturers like Glidden, Sherwin-Williams, and Benjamin Moore, they succeeded with, **Rhoplex AC-33**, an acrylic-emulsion paint binder. Rhoplex AC-33 was introduced to the paint industry in 1953 for use in making the first commercial acrylic water-based paints.



Of course, the introduction was not easy. Rohm and Haas had to demonstrate to its customers the advantages of Rhoplex, which included greater durability and smoothness of application. But after several years in the trenches, working with the customers, solving technical problems, and making new formulation after new formulation, acrylic-emulsion paint binders finally became a permanent fixture in the paint industry.

By 1973, paints made from acrylic emulsions were leading the interior semi-gloss market in the United States and five years later had essentially replaced oil-based exterior paints.

Hollow Spheres



A paint's opacity is its ability to keep light from passing through. A high-opacity paint will hide what it's covering well, requiring fewer coats. The traditional paint opacifier was titanium dioxide, and it was very expensive. Rohm and Haas joined the race

History Spotlight
The Company Logo

in the 1970s to mimic the effects of titanium dioxide with a more economic technology. Eight years in the making, Rohm and Haas introduced its revolutionary "hollow sphere" technology to the paint industry in 1982. The product, named **Ropaque**, worked by trapping tiny air voids in polymer film. These voids, or hollow spheres, scatter light, preventing it from passing through. Ropaque enabled paint manufacturers to formulate their paints with less pigment and binder without compromising performance.

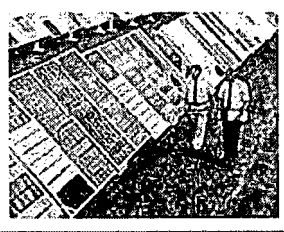
The Paint Quality Institute



By 1989 Rohm and Haas paint ingredients were in 85% of the exterior acrylic paints sold in the United States. But the question, "Why choose acrylic paints, which often cost more, over other types of paints?" was still on consumers' minds.

Rohm and Haas paint ingredients produce very high quality paints, which cost a little more but are more cost-effective in the long run because they last longer and look better.

Rohm and Haas wanted to work with its customers — paint manufacturers like Glidden and Sherwin-Williams — as well as with consumers, to educate them about the advantages and superior quality of acrylic paints. To this end, the Rohm and Haas Paint Quality Institute was created to educate consumers on the acrylic advantage and the importance of using quality paints.



↑ TO TOP

You are here [Our Story](#) : [Innovation](#) : Revolutionizing Paints

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Germany, who first reported the production of a solid acrylic polymer in 1901 and developed a commercial synthesis of acrylate esters in 1927 [11,12]. It also does not review the incredible developments that have taken place with organic and inorganic pigments, although good accounts of these exist already (e.g. [13,14]).

The conservation concerns with acrylic paint media tend to fall into three categories and will be presented as such: the Development of Waterborne Acrylic Artists' Paints, Paint Properties, Aging Properties and Cleaning Issues.

THE DEVELOPMENT OF WATERBORNE ACRYLIC ARTISTS' PAINTS

Henry Levison, a chemist-turned-paint maker, founded the company Permanent Pigments in 1933, which produced the first line of waterborne acrylic emulsion paints called Liquitex® in 1954 [14]. He often supplied artists in exchange for soliciting their advice and occasionally hiring them as consultants or staff. The development of Liquitex® came a few years after the introduction of the first artists' acrylic paint, Magna®, by the paint makers Leonard Bocour and Samuel Golden in 1947-49. Magna® acrylic paints were solution paints, and quite distinct from waterborne emulsion paints. In practical terms, Magna® dried quickly by evaporation of organic solvent, remained resolvable in many hydrocarbon solvents as well as further layers of paint and could be blended with oil paint [15,16,7]. In contrast, the drying process of emulsion paints involves a complicated coalescence of emulsified polymer spheres after an initial evaporation of water; these paints become insoluble in water - and further layers of emulsion paint - after they have dried.

Confusingly, many terms are used to refer to waterborne acrylic paints, such as 'acrylic paints', 'acrylic emulsions', 'latex', and 'polymer colours'. In fact, technically, they are 'dispersions' rather than 'emulsions', because they are composed of tiny beads of solid, amorphous polymer suspended in water. The fact that these paints could be diluted and thinned with water, instead of mineral spirits, made them - and continues to make them - very appealing to artists. The raw polymer emulsions used by artists' colourmen and paint makers were frequently those from Rohm and Haas' Rhoplex® series of products (known as Primal® in Europe), such as AC-22, AC-33, AC-234 and AC-634. Rhoplex® AC-33 first became available in the 1953. All of these emulsions were copolymers, utilizing the harder methyl methacrylate (MMA) and softer ethyl acrylate (EA) to create the required working properties (e.g. flexibility) and durability for house paints, their primary market. Since the end of the 1980's many of the resin formulations have changed to a poly (*n*-butyl acrylate/methyl methacrylate) copolymer, such as Rhoplex® (or Primal®) AC 235. These films tend to be slightly tougher and more hydrophobic than the pEA/MMA resins, making them more durable to outdoor exposure. Styrene has sometimes part or wholly replaced the MMA component to save manufacturing costs [17,12,18].

ADDITIVES

Acrylic emulsions contain a multitude of additives that determine the performance properties of the paint, from shelf life to application and longevity, to health and safety properties [19,20,21,18,22]. They are included at two distinct stages of production: during the manufacture of the emulsion polymer and during the formulation of the paint itself. With the exception of a few volatile additives (see below), all additives remain in the dry paint film. Research into their interaction with the binder is therefore necessary for a complete understanding of the aging properties and effects of treatment on acrylic emulsion paints. However, almost nothing has been achieved towards this, either analytically or from manufacturer's information, on their precise identity. While the paint formulator knows the basics of these materials, proprietary materials are frequently incorporated by the manufacturer of the additive, and the additives themselves are constantly changed to meet the needs of the large coatings industry [20,23].

Additives in the emulsion binder

- *Initiators*: used as a source of free radicals to initiate the polymerization process - in which monomers condense to form the polymers. These are most often persulfates, e.g. potassium persulfate [24], which

The Conservation of Acrylic Emulsion Paintings: A Literature Review
By Elizabeth Jablonski, Tom Learner, James Hayes and Mark Golden

ABSTRACT

Acrylic emulsion (or more accurately dispersion) paints present major challenges to paintings' conservators, yet remarkably few studies of these materials have been published. The intent in this paper is to present the conservation information that does exist in a concise format to expedite much needed further discussion and research by conservators, paint manufacturers and artists. Brief descriptions of the development and analysis of acrylic emulsion paints are given, but the focus of this review is on conservation concerns, in particular issues surrounding the paints' properties, ageing and cleaning.

INTRODUCTION

Acrylic emulsion artists' paints were received with much fanfare and excitement in the 1950's and 1960's. They embodied the characteristics that many artists had been searching for at that time, affording a means of expression that was distinct from oil painting and its associated history and traditions. As Kenneth Noland expressed it, "the materiality and actual work process became more *present* [1]." These synthetic paints produced films of great clarity and phenomenal elasticity, were easy to manipulate, could be painted directly onto supports, dried quickly, were thinned with water and exhibited high resistance to ultraviolet degradation. John Hoyland recalled "I remember reading articles in magazines. They talked about the radiance of [acrylic paint] and the fluidity of it... and that it would never yellow. It seemed exciting in the way people got excited about the use of plastics, aluminium and other industrial materials [2, p. 101]". And Helen Frankenthaler, who switched from using oil paints to acrylic emulsions in the early 1960s, said:

"I changed to acrylics for a number of reasons. Once, I was told that they dry faster, which they do, and that they retain their original colour, which they do. I would say durability and light and the fact that one can use water instead of turpentine: all that makes it easier given the abstract image.... As painting needed less and less drying time, depth, and so forth, the materials came along that made that more obvious [3 p. 82]".

In spite of their outstanding mechanical and aging properties, acrylic emulsion paintings do suffer damage, often through external influences. Within the conservation profession, concerns were soon raised as some of these newly painted works began to require cleaning and repair [4,5]. Similar themes were discussed in the following decades [6,7,8].

Essentially, three fundamental problems were identified. The first was that most conservation treatments had been designed for traditional oil paintings and were found unsuitable for acrylic emulsion paintings, due in particular to the high sensitivity of these synthetic paints to the majority of organic solvents and heat. The second was the complete lack of knowledge about these acrylic emulsion systems, especially the complexity and constant changes to the formulas, with insufficient information coming from the manufacturers of both raw materials and artists' paints. And third, damage may be especially noticeable in colourfield or monochromatic paintings, as a disruption to the delicate surface texture, colour or gloss [1,8,9], all of which are often integral to the artists' intent and can be altered by even the slightest contact. Even small damages can therefore soon become 'unacceptable'. Since remedial treatment is so difficult with acrylic paintings, preventive conservation is crucial [10].

In general, very few studies of the conservation of acrylic emulsion paintings are published. Instead, concerns tend to be communicated through informal discussion. The intent in this paper is to review the available information from conservation literature and to encourage further discussion and research by conservators, conservation scientists, paint manufacturers and artists. It should be stressed that this review only takes into account publications in the English language and a broader understanding of the subject would be possible from surveying material written in other languages, in particular the work of Röhmer in

COMPETITIVE IMPLICATIONS OF ENVIRONMENTAL REGULATION IN THE PAINT AND COATINGS INDUSTRY

This case study was prepared by Ben Bonifant, Management Institute for Environment and Business. The research was conducted in collaboration with the U.S. Environmental Protection Agency and Hochschule St. Gallen. Copyright 1994 by MEB. The author gratefully acknowledges the guidance that was provided by Claas van der Linde of Hochschule St. Gallen.

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EXECUTIVE SUMMARY

Introduction

During the late 1980s and early 1990s, industrial users of paint often faced strict environmental regulation on their operations because of the large volumes of solvents released in the surface coating process. These manufacturers turned to their paint suppliers demanding products which not only performed acceptably in all traditional characteristics but also incorporated significantly reduced amounts of organic solvents. U.S. paint manufacturers' need in the 1980s and 1990s to provide innovative solutions offers an example of how suppliers can be affected by regulations aimed at their customers. As regulations were promulgated, industry managers were forced to choose appropriate areas to dedicate development resources. Factors influencing these decisions included expected development time and costs, resource availability of the innovating firms, and anticipated market size for innovative products. Where the paint companies successfully developed compliant coatings, their customers were provided with opportunities for compliance at dramatically lower cost than would have been incurred in adopting control equipment solutions. Where paint manufacturers possessed technologies which were less environmentally damaging, the regulations spurred experimentation by their customers and in some cases allowed entry into markets where the suppliers had previously not participated.

Market Overview

Worldwide production of paints and coatings was estimated to be \$35 billion in 1990 with North American firms manufacturing almost 40% of this total. The market comprised three types of coatings: those sold to contractors and homeowners for interior and exterior wall covering, those sold to industrial manufacturers for product coatings, and those sold for special purpose applications. The first segment, known as architectural coatings was the largest making up 38% of the market. Original equipment manufacture (OEM) product coatings made up 32% of the 1990 U.S. market, and special purpose coatings made up 21%.¹ Special purpose paints were on items outside of a manufacturing site and for industrial purposes. Autobody refinishes made up almost half of this segment.


1. The U.S. Department of Commerce categorized an additional \$910 million market in its measurement of "Paints and Allied Products." Making up 7.3% of the total, allied products included dopes, thinners, pigment dispersions, and other similar products.

Three types of firms produced paints. The largest suppliers such as PPG Industries, Sherwin Williams, and ICI-Glidden provided coatings to several areas of the market. These firms dedicated large resources to maintain strong positions in large market segments. Often, they had integrated upstream to independently produce resins for their formulations or they had integrated downstream to market their products directly to customers through company owned stores.

A second type of firm provided specialized coatings to narrow segments of the OEM or special purpose markets. Suppliers to the largest market segments (BASF in automotive manufacturing and refinishing for example) ranked among the largest paint firms. Those which concentrated on smaller segments such as marine coatings or wood furniture manufacturing sometimes dominated in their markets, but typically ranked as only mid-sized suppliers.

A third type of firm focused only on architectural coatings. Although major paint companies including Duron and Benjamin Moore had achieved large industry positions producing primarily architectural coatings, hundreds of small firms also supplied this segment; most with revenues of less than \$5 million.

Environmental Regulations

 Paints were applied to protect and enhance the appearance of a surface. Solvents in the coating facilitated application and assured a smooth finish, but were not part of the final coating. Eventually, all of the solvent evaporated from the coating and was either captured and controlled or was released as air emissions. In 1985, surface coating operations accounted for 27 % of all industrial emissions of volatile organic compounds (VOCs). When exposed to sunlight, these VOCs contributed to the formation of tropospheric (lower atmosphere) ozone. Regulations aimed at reducing tropospheric ozone levels targeted precursors including VOCs.

With the passage of several state regulations in the 1960s and 1970s as well as the Clean Air Act Amendments of 1977, users of industrial coatings began to be regulated in the United States. In accordance with the Clean Air Act Amendments of 1977, the EPA provided Control Technique Guidelines (CTG) and New Source Performance Standards (NSPS) as aids for the state regulators and

permit writers. These documents focused on individual types of manufacturers and provided guidance in methods of reducing emissions for their industry. Typically, they offered practical limits on the VOC content of coatings. Alternatively, manufacturers who chose not to change coatings could comply by adding control equipment to their operations.

While the U.S. led other industrial countries in the regulation of coating application, Germany, the Netherlands, and the U.K. began adopting similar regulations in the late 1980s. As in the U.S., these regulations focused on OEM operations. While these regulations had an important effect on several industries in Europe, the U.S. regulations remained the most strict.

In the OEM segment, competition in the paint market had always been based on the manufacturers' ability to provide a coating which satisfied the variety of customer performance requirements. Environmental regulation defined a new type of performance need - lower solvent content. As a result, the goal of reducing VOC emissions by reducing solvent became the primary focus of research and development in the U.S. paint industry throughout the 1980s and early 1990s. Paint suppliers hoped to provide formulations which employed lower amounts of solvent and thus could be used without control equipment. Therefore, without being directly regulated themselves, paint suppliers were dramatically affected by the regulations. As suppliers working under existing competitive systems, the paint companies had strong incentives to provide low cost solutions to their clients' regulatory requirements.

By 1991, the annual EPA survey of sources of VOC emissions demonstrated that paint regulations had had an impact. In that year, 1.86 million metric tons of VOCs were emitted by industrial surface coating operations. This represented a 15 % reduction from the 2.2 million metric tons emitted in 1986. During the same period, other industrial sources of VOC emissions increased by 5 %.

Industry Performance at the Time of Regulation

U.S. paint manufacturing showed modest sales increases in the late 1980s with compound annual growth of approximately 4% between 1986 and 1991 (22% overall growth during the same period VOC emissions fell 15 %). In 1991, the Department of Commerce reported that the value of shipments had

reached \$12.9 billion. Also during the late 1980s, the U.S. share of world exports held firm at approximately 9 % and the balance of trade grew substantially from \$150 million to \$320 million.

Effect of Regulation on Competitiveness

The influence of environmental regulations on the international competitiveness of the U.S. paint firms was modest in the early 1990s. At that time new regulations were just beginning to take effect in a few European countries and no regulations existed in Japan for coating processes. However, it can be seen that the U.S. position in world trade in paints remained strong even as manufacturers were compelled to dedicate increasing resources to low VOC developments. These developments were likely to find increasing international markets as regulation took effect in other countries.

In at least one case, the more stringent environmental regulations in the U.S. were a factor in encouraging the transfer of technology from Europe to the U.S. market. The manufacturer, having dedicated more than a decade of research efforts to water-borne automobile coatings, possessed a technology which was judged to be superior by several North American auto manufacturers as they explored their options under new regulations. The coating manufacturer entered a licensing arrangement with existing suppliers to access these customers. As regulations began to focus on automobile refinishes, the supplier was preparing to enter the market independently.

Within the U.S., the industry's response to regulations on different segments of the market is instructive on how supplying industries react to pending regulation. When California regulated wood furniture manufacturers, the relatively small coatings suppliers were unable to dedicate large resources to the demands of a regional part of their markets. Facing few alternatives to adopting expensive control equipment (in addition to high wage rates and other regulations), many manufacturers left the region. In time, and facing regulations on wood furniture manufacturers across the U.S., coatings suppliers were able to develop acceptable water-borne systems. Similarly, when the large automobile coatings market faced regulation suppliers rapidly developed alternative products.

Regulations on architectural coatings drove results which demonstrate the differing responses of suppliers depending on their resource availability. When architectural coatings were regulated in California, many small suppliers fought bitterly against the concept of reduced VOC requirements. Meanwhile, large producers (even in other parts of the country) anticipating a huge developing market opportunity dedicated large resources to innovative products which could be used with less adverse impact on the environment.

The characteristics of innovations in the paint industry have implications for any other regulated area. Here, as in many other areas, the innovations have not occurred within the regulated industry itself. Instead, new approaches were developed by suppliers at least one step up the value chain. In the case of new resin systems, the new developments were several steps upstream. These upstream industries must choose how to dedicate scarce resources. They will dedicate these resources to methods of lower cost environmental compliance when the regulations are structured to allow creative methods, the market for innovations is large relative to the required development investment, firms possess the needed resources, and the decision makers in the regulated area are receptive to new approaches of achieving compliance.

INDUSTRY STRUCTURE

Product

Product Description

The earliest development of the paint industry in the U.S. began with the first needs for coating and protecting residences. Paint companies were primarily pigment manufacturers who prepared powders of coloring by grinding naturally occurring materials. Until the middle of the nineteenth century, professional painters would combine pigments with an oil or varnish and thinners. In 1867, D.R. Averill prepared the first generation of ready mix paints. These emulsions of pigments in oil, zinc oxide, lead acetate, and lime water were initially found to be unacceptable by many painters. However, they set the stage for later developments by other manufacturers which increased the consistency and the quality of the product.² These developments dramatically changed the market for paints. Consistency began to depend on the manufacturer and not the skills of the journeyman painter. Also, the door was opened to less sophisticated buyers performing do-it-yourself activities on their homes.

The large market for coatings of rail cars and early automobiles spurred the initial growth in original equipment manufacturer (OEM) markets. Manufacturers began searching for innovative resins which could provide coatings which were more durable, faster drying, or less costly. Early substitutions for resins included coumarone, pheno-formaldehyde, and nitrocellulose. Concurrently, new solvents derived from coal and petroleum processes were being utilized. In the period following World War II, the technical sophistication of manufacturing paint increased substantially. As a result, the proliferation of small start up paint companies had decreased dramatically. From that time forward, the paint industry experienced a continuing consolidation.

The paint and coatings market was a large diverse industry in the early 1990s with a wide variety of applications and customers. OEM paint markets naturally followed the growth and decline of their manufacturing customers. Similarly, markets for architectural coatings were closely tied to construction activity. Not surprisingly then, the market for paints and coatings has been closely tied to the movements

² Sherwin Williams, Annual Report 1991, "125th Anniversary 1866-1991

of the economy as a whole. Within the market, share shifts from low solids to high solids and water-borne coatings were the most notable developments in the early 1990s. Systems requiring no solvents, radiation cured and powder coatings, were also showing growth significantly greater than the rest of the market.

Once applied, paints and coatings formed thin continuous layers used to protect and decorate surfaces. As supplied to the user, paint and coatings were primarily made up of three components: resin, pigments, and solvents. After application and drying, only the resin and pigment systems remained in the paint as the solvent evaporated. The resin was a polymer material which made up the primary substance of the coating and provided its protective properties. Several polymers were employed by paint manufacturers for resin systems including alkyds, urethanes, acrylics, and polyesters. Pigments were carried in the resin to offer decorative features and in some cases assist in protecting the substrate from UV degradation. Inorganic materials such as titanium dioxide and aromatic organic materials including phthalocyanines were examples of widely used pigments.

Solvents were used in paints solely to facilitate application of the resin and pigment system to the substrate. Originally mixed into a powdered resin/pigment system at the site of application, the solvent most commonly used in the late nineteenth century was turpentine. Fossil fuel distillates began to be utilized as their availability became more widespread in the early 1900s, and following developments in the last half of the twentieth century, there was a progression toward greater use of water. By 1990, in most applications, solvents constituted 10% to 50% of the coating system; however in a few areas such as wood furniture coatings, solvents could make up 75% of the system.

Application of paints demanded a tradeoff. High solvent content could yield low viscosity and allow rapid application. However, this could also lead to dripping and running. With lower solvent content, the paint was not only more difficult to apply but it might not provide an acceptably smooth finish. As a result, paint formulators typically used several solvents. The use of water as the primary solvent, for example, did not necessarily mean that some petroleum derived solvents were not employed as well.

Substitutes

Because the paint and coatings industry was defined to include almost all types of chemical surface coverings, there were few substitutes for the products of this industry. Significant trends toward greater use of wallpaper or pre-treated paneling could have had a measurable effect on the architectural coatings market, but dramatic changes in consumer preferences in these areas were unusual. Similarly, for OEM (original equipment manufacturer) coatings, a dramatic shift in styles toward materials which did not require coatings would be required to significantly affect the size of this industry. Had, for example, the DeLorean automobile with its stainless steel body panels initiated a national trend, the \$970 million market for automobile coatings might have been threatened.

Production Process

Paint manufacturers were primarily formulators. They determined the combination of raw materials which satisfied the user's coating needs and supplied that formulation to their customers. The manufacturing process was a series of steps aimed at providing a uniform mix and sizing of component materials. There were five primary steps in this process. A premixing step where pigments, resins, and some solvents were combined, produced a paste of homogeneous composition. The pigment particle size was then reduced in a dispersion process. The next two steps involved thinning the material with additional solvents and then filtering the resulting product. Finally, the paint was packaged for delivery to customers.³

As a rule, only the largest paint firms performed significant levels of research and development. These development efforts involved formulating combinations of proprietary and commercial resins, solvents, pigments, and additives and performance testing. In the most concentrated markets such as automobile or appliance coatings, the manufacturers worked closely with the customer to develop a coating which provided a customized combination of performance characteristics.

3. Randall, Paul M "Pollution Prevention Methods in the Surface Coating Industry," *Journal of Hazardous Materials*, Elsevier Science Publishers B. V. I Amsterdam, p. 282

Smaller firms relied on raw material manufacturers to provide formulation assistance. Lacking the resources to dedicate to basic research and development, these firms followed very closely the recommendations of their suppliers concerning constituent combinations.

Economies of Scale

Scale economies were modest in paint production because fixed costs which could be reduced by increasing volume were limited. Notably, spreading of research and development costs (4-6% of revenue for most large producers in the U.S.) and advertising costs (approximately 1% of architectural coatings sales in the U.S.) provided an advantage to larger firms. In operations, increasing batch size had the expected advantages in reducing average manufacturing costs. However, large manufacturers had limited advantage over regional producers in this area because the cost of distribution quickly overtook the advantage of increasing batch size. All of the largest manufacturers had adopted strategies of regional manufacturing to limit distribution costs.

Despite the limited economies of scale, the paint and coatings industry was consolidating (in terms of establishments) in both the United States and in Europe. In 1980, it is estimated that there were more than 1800 firms manufacturing paint in Europe. By 1990, that number had fallen to 1500 (an annual decline of more than 2%).⁴ In the United States, consolidation was also occurring. With a reduction of almost 1% annually, the number of firms producing paint in the United States declined from 1600 in 1977 to 1400 in 1992.⁵

Entry or Exit Barriers

Two significant barriers existed for new suppliers attempting to gain a position in these markets. The first barrier, particularly important in OEM markets, was the need for relationships with buyers which allowed joint development of new products. Buyers had highly specialized requirements which demanded

4. Information Research Limited. "A Profile of the West European Paint Industry, Ninth Edition," London, 1990

5. Rauch Associates, Inc. "The Rauch Guide to the U.S. Paint Industry," Bridgewater, N.J., 1990

that manufacturers dedicate significant technical resources to match coating characteristics to application needs. Often, the coatings were formulated for specific products produced by individual manufacturers. Smaller companies lacked the access to large OEMs and therefore could not anticipate their developing needs. The second barrier for entering large OEM markets was the requirement of coordinated development with manufacturers of application equipment. Product development required familiarity with the systems as well as access to advance information on innovations occurring in application technology. Coordinated development ultimately emerged where large buyers drove cooperative research between the dominant coatings suppliers and the major providers of application equipment. For example, in 1989, Union Carbide developed the Unicarb system, an innovative method of paint application for industrial uses (discussed further in a later section). Bringing the product to market required coordinated development with Nordson, a spray equipment manufacturer as well as with coatings suppliers such as Akzo, BASF, Gaurdsman, Lilly and PPG Industries.⁶

Buyers

Buyer Description

Customers required coatings to provide protection and enhance appearance. Additionally, depending on the surface to be coated, customers made selections based on price, ease of application, abrasion resistance, weather resistance, smoothness of finish, and non-toxicity. After the mid-1970s, customers also demanded that products comply with a variety of local, state, and national regulations requiring that coatings not exceed specified levels of volatile organic compounds (VOCs).

In a sense, the coatings market could be characterized as a continuum with one end occupied by the fragmented, poorly informed buyers undertaking infrequent home improvements. Many suppliers with products of varying quality supplied this end of the market; mass marketing skills and strong distribution channels represented strategic assets. On the other end of the continuum, market segments were dominated by a few highly informed buyers of coatings for original equipment manufacturers. Technical

6. "Supercritical CO₂ As a Solvent: Update on Union Carbide's Process." *Modern Paint and Coatings*, June, 1990

abilities to match product performance to narrowly defined customer needs and direct selling skills were required for success in these markets.

Distribution Channels

In the United States, architectural coatings made up 38% of the total 1990 market (table 7). Large firms successfully supplying this segment possessed strong commercial distribution systems. The three primary channels of distribution were:

- * Company owned stores
- * Distribution contracts with large mass merchandisers
- * Lumber and specialty retail stores

Additionally in the 1980s, the rapid development of large home improvement centers such as Home Depot had presented an additional growing channel to the "do it yourself" part of the market.

A number of large companies such as Sherwin-Williams operated company owned stores in order to control product presentation and achieve additional trademark recognition through buyer familiarity with the store and its signage. Smaller firms such as Dunn Edwards and Duron had achieved similar advantages on a regional level. Other firms though, such as PPG with its Lucite and Olympic paints, developed strong brand recognition while selling through national retailers.

Direct sales and specialized services were used in selling to the OEM market because there were only a few very knowledgeable buyers. Because a small number of people had control over very large purchase decisions, the paint companies devoted significant resources to keeping these individuals informed of technological and performance developments.

Suppliers

The primary suppliers to the paint and coatings industry were producers of synthetic chemicals who manufactured resins, solvents, and pigments, usually from coal and petroleum feedstocks. International

firms such as Rohm & Haas, Reichhold Chemical, Dow Chemical, and Union Carbide Chemicals and Plastics Co. were important suppliers to the industry throughout the world.

Many of the largest U.S. suppliers of coatings including PPG, Sherwin Williams, and Lilly Industries had integrated upstream into manufacturing proprietary resins. Their innovations in basic resin chemistry had provided them with strategic advantages in several market segments. PPG's development of electrodeposition coatings for automotive underbodies in the 1970s and Glidden's developments in latex paints in the late 1940s were examples of innovations in resin chemistry which had allowed a firm to establish a dominant position in a market segment which lasted for decades.

Environmental Regulation

Environmental risk analysis

Three types of regulations affected the U.S. paint industry:

- * Production regulations required paint manufacturers to track their emissions more closely, invest in control equipment, and explore opportunities for waste minimization.
- * Site restoration regulations involved the identification and clean-up of previously disposed waste. Although this type of regulation was not unique to the U.S., the Superfund requirements were the most far reaching.
- * Users of paints and coatings were regulated to limit the emissions resulting from application processes. In many instances, the most cost effective means of remaining in compliance was to adopt coatings with lower solvent content. Paint manufacturers were, then, indirectly affected as their customers pressured them to provide compliant coatings.

As much as 70% of some coatings were made up of organic solvents. Therefore, the paint industry and its customers maintained important use and disposal responsibilities. Limitation of emissions was desired because of the role solvents played in the formation of low level ozone. In the troposphere (lower

atmosphere), the formation of ozone was undesirable because it was thought to cause adverse health effects and harm vegetation.⁷

The solvents were volatile organic compounds (VOCs) which were precursors to the formation of ozone. In the presence of sunlight, VOCs reacted with nitric oxide (NO) resulting in increased levels of nitrogen dioxide (NO₂). Since the ratio of NO to NO₂ was in equilibrium with the formation of ozone, the increased level of NO₂ led to increased levels of ozone.⁸ Regulations aimed at reductions of tropospheric ozone were focused on reducing emissions of the precursors.

In 1991 35% of all VOC emissions were thought to result from mobile sources, primarily automobiles. The remaining 65% occurred at stationary sources and were associated with solvent use, hazardous waste disposal, surface coating, petroleum marketing, petroleum refining, and chemical manufacturing. Surface coating contributed 11% of all VOC emissions.⁹ As a result, paint users were targeted for emission reductions in a series of air regulations

1991 U.S. National VOC
Release Estimates

Source	Releases (million ton)	Share
Industrial Releases (excluding coatings)	6.0	35%
Transportation Sources	5.1	30%
Surface Coatings	1.9	11%
Forest Fires and other burning	1.0	6%
Solid Waste Disposal	0.7	4%
Fuel Combustion	0.7	4%
Miscellaneous Organic Solvent Use	1.6	9%

Source: U.S. EPA
Figure 1

Severity and Impact of Regulations

In the U.S., paint manufacturers claimed that the cost of compliance with site restoration regulations was unnecessarily high. Following a survey of its members, the National Paints and Coatings Association

7. Reducing the formation of ozone in the troposphere should not be confused with efforts to stem destruction of the ozone layer in the stratosphere (where ozone protects the earth from harmful ultraviolet radiation).

8. U.S. Environmental Protection Agency, "Control Techniques for Volatile Organic Compound Emissions from Stationary Sources, Third Edition," 1986, p. 2-4 through 2-6

9. U.S. Environmental Protection Agency, "National Air Pollutant Emission Estimates, 1900 - 1991." October 1992

concluded that its members were spending \$7 million a month on Superfund negotiations in 1992.¹⁰ Strikingly, the organization concluded that of \$600 million spent prior to the survey, \$400 million had been spent on transaction costs (litigation and administrative fees). Only \$200 million had actually been spent on cleaning up sites.¹¹ While these costs represent less than 1% of annual revenue for the industry, they were not evenly spread across manufacturers. The survey found that 33 % of respondents were not affected by any Superfund clean-ups, and an additional 26% were involved at only one site. The costs incurred on different sites varied dramatically with \$50,000 to \$150,000 typically being required for a paint manufacturers experience on a single site (where they were often small contributors to the total volume of waste disposed)¹²

The operating cost of compliance with production regulations was modest. In 1989, U.S. paint manufacturers had capital expenditures for pollution abatement equipment of \$9 million while total capital expenditures were \$271 million (thus total capital expenditures were less than 2% of sales for the year and capital expenditures for environmental controls were 3 % of that).¹³

Pollution abatement operating costs were higher, but still represented only a small part of the overall cost of paint production. In 1990, U.S. paint and coating suppliers incurred \$91 million in pollution abatement operating costs with \$43 million of this going for the disposal of hazardous wastes. The total operating costs for pollution abatement represented approximately 0.7% of the value of shipments for 1990.¹⁴

10. Superfund refers to the Comprehensive Environmental Response Compensation and Liability Act. Passed in 1980, this legislation required that manufacturers fund remediation of sites in which they had disposed materials,

11. National Paint & Coatings Association, "Improving the Superfund: Correcting a National Public Policy Disaster," 1992

12. National Paint & Coatings Association, "improving the Super-fund: Correcting a National Public Policy Disaster," 1992

13. U.S. Department of Commerce, "Manufacturers' Pollution Abatement Capital Expenditures," 1990

14 U.S. Department of Commerce, "Manufacturers' Pollution Abatement Capital Expenditures," 1990

From a strategic standpoint, production and remediation expenditures represented costs which needed to be controlled. In most cases, however, responsibility for these costs remained in the environmental affairs, government affairs, and legal departments of paint manufacturing firms. By comparison, the regulations on paint users put new demands on broad areas of the organization. The companies' customers were demanding fundamental changes in formulation of the product. As a result, the sales, research, production, and purchasing organizations were affected. The upper management of the firms were faced with decisions of resource allocation to determine how best to respond to this major change in the industry's markets. For these reasons, the regulations affecting the use of the product were the most important environmental issue affecting the paints and coatings industry in the 1990s. Figure 2 summarizes the implementation of regulations aimed at controlling VOC content in the leading paint supplying countries. The following sections discuss these regulations and the characteristics of competition in each of these nations.

Timeline of Important Regulatory and Environmental Events

- | | |
|------|--|
| 1754 | First U S paint manufacturer, Davoe Raynolds, is founded |
| 1867 | D.R. Averil leads development of "ready-mix-paints" |
| 1948 | Glidden introduces water-borne housepaints |
| 1966 | California adopts Rule 66 regulating VOC content of paint |
| 1977 | U.S Clean Air Act Amendments require development of Control Technique Guidelines for industrial coating operations. |
| 1986 | TA Luft regulates industrial coating operations in Germany |
| 1986 | Dutch government adopts KWS2000 targeting 50% reduction of VOC emissions by 2000 |
| 1990 | U.K. passes Environmental Protection Act requiring the development of Guidance Documents for permittees regulating coating operations |
| 1990 | U. S. Clean Air Act Amendments target VOC reductions in eleven previously unregulated industries as well as requiring the development of a National Rule on VOC content of architectural coatings. |
| 1991 | 23 countries sign United Nations European Commission for Europe protocol targeting 30% VOC reduction by 2000 |

Figure 2

COMPETITION

United States

Competitiveness Overview

The 1990 worldwide coatings market was estimated at \$35 billion. The United States and Canada made up almost 40% of this total with an estimated market of \$13.5 billion. Western Europe and Japan followed with market sizes of \$11.5 billion and \$4.5 billion respectively.¹⁵ The U.S. Department of Commerce estimated the production of paint and allied products at \$12.8 billion in 1990, having grown from a value of \$10.2 billion in 1985 (an annual growth rate of 4.6%) (table 7).

Because there was only a modest scale economy in the manufacturing process for paint, and shipping costs could quickly overwhelm the value of the product if the material were to be transported over long distances, firms strategically located manufacturing facilities to optimize the trade-off between scale advantages and increased shipping costs. Even within the U.S., firms produced in multiple locations. For these reasons most countries also shipped very little paint internationally, and the volume which was exported was dominated by shipments to neighboring nations.

This also means that trade data could only be used to get a first indication of a nation's competitive position. However, those nations which had large shares of the world trade in paint along with positive trade balances appear to have been the home for innovation and development in this industry. In 1990, the U.S. had a 9.2 % share of world export of paints ranking behind West Germany at 24.6%) the Netherlands at 10.7%. and the U.K. at 10.1%. However, the U.S. had the second strongest balance of trade in paints in 1990 at \$3 18 million trailing behind only West Germany at over \$800 million (tables 1-3).

15. "In Paints and Coatings, Change is the Only Constant," Chemicalweek, October 31, 1990

Leading Firms

Manufacturers in the paint industry fell into three segments.

- * Diversified Suppliers
- * Application Specific Suppliers
- * Architectural Coating Suppliers

Diversified Suppliers

The largest producers, characterized in the U.S. by PPG and Sherwin Williams, manufactured coatings for a variety of end-use areas. These firms held large shares in many of these segments, but also participated in areas where their share was very small, often after having acquired firms focused on these areas. At times, these firms unified the strategic management of their acquisition, but manufacturing facilities and sales efforts often remained focused on narrow market segments. In the late 1980s and early 1990s, a few large firms began rationalizing their businesses by returning to more narrow market segments. For example, in 1993, Lilly Industries and ICI-Glidden reinforced areas where each firm possessed a strong position. ICI traded its liquid industrial coatings business (and cash) for Lilly's packaging coatings business, an area where ICI was a recognized world leader.¹⁶

U.S. Total Value of Shipments of Original Equipment Manufacturer Paint

Category	1990 Value (million)
Transportation Coatings:	
Automobile Finishes	\$967
Truck, Bus, and RV Finishes	\$199
Other Transportation Finishes (inc. aircraft and rail)	\$77
Container and Closure Finishes	\$487
Metal building Product Finishes	\$345
Wood Furniture	\$339
Nonwood Furniture and Fixture Finishes	\$251
Machinery and Equipment Finishes	\$200
Paper, etc. Finishes	\$89
Wood and Board Flat Stock Finishes	\$67
Appliance, Heating Equipment, and Air Conditioning	\$65
Electrical Insulating Coatings	\$28
Powder Coatings	\$244
Other Industrial Product Finishes	\$327

Source: U.S. Department of Commerce. Current Industrial Reports, Paint and Allied Products. 1991

Figure 3

16. The Glidden Company, "ICI Paints Agrees With Lilly Industries on Business Transfer," Company Press Release, March 2, 1993

Application Specific Suppliers

Many coatings firms focused exclusively on narrow segments of the OEM or special purpose market. Working closely with their customers, these firms developed technical expertise in balancing the various needs of these industrial manufacturers. Depending on the segment size, these manufacturers could rank among the largest in the industry. BASF and DuPont, for example, sold coatings primarily to automobile producers and refinishers. Achieving large shares in these markets made these firms among the largest coatings suppliers in the world. In other segments, even the leading suppliers were fairly small. With revenues below \$100 million, companies such as Ameron, or Guardsman were dwarfed by the largest coatings suppliers, but they held large market shares in specific segments such as aerospace coatings, or wood furniture finishing.

In the OEM coating segment, almost all sales were made directly to the customer through the producer's sales force. In addition to providing specific formulations for the customer's needs, paint suppliers provided a variety of services to their largest clients which could encompass all aspects of coating the customer's products. PPG, for example, assisted in incorporating its paints into customers' existing equipment, advised customers on other types of equipment to use, and in some cases, even managed the entire painting process on a contract basis.¹⁷

The most consolidated areas of the OEM market were automobile with three primary suppliers (PPG, BASF, and DuPont), can coating with two primary suppliers (ICI and Dexter), and wood furniture finishing with four primary suppliers (Lilly Industries, Gaurdsman, Valspar, and Akzo-Reliance). These segments made up 7.8 %, 3.9%, and 2.8 % of the total market for coatings, repectively .

During the 1990s, strong firms participated in foreign markets in ways other than direct export, primarily by purchasing existing assets from local owners. In OEM coatings, U.S. firms had followed their clients in their pursuit of global markets. As automobile, beverage can, and appliance manufacturing firms

17. PPG Industries, Inc., William V. Warnick - Director, C&R Manufacturing, Interview Pittsburgh, PA, February 25, 1993

located operations internationally, the coating companies serving those firms purchased local firms to maintain longstanding relationships. Technology was transferred to the local facilities from the U.S. and applied in existing equipment. PPG, for example, became one of the five largest paint suppliers in Europe through strategic acquisitions in Italy, Germany, Spain, France, and the U.K. A substantial share of this revenue resulted from sales of electrodeposition coatings for automobile underbodies, technology developed in the U.S. but later transferred throughout the world.

Architectural Coatings Suppliers

The third group of companies were those providing architectural coatings (interior and exterior housepaints) to a regional market. While a few of these firms provided paints to some OEM or specialty segments, they focused primarily on regional sales to trade and consumer buyers. Larger firms in the U.S. included Benjamin Moore (\$350 MM 1990 sales), Kelly Moore (\$175 MM), and Pratt & Lambert (\$140 MM) but hundreds of companies fit into this category with most having revenues of less than \$5 million. While a few of these firms were very strong on a regional level, they all faced significant competition from diversified national firms. As a result, the smaller producers competed in niche markets, by providing private label products to smaller retailers, and by pursuing continual cost reductions. The strength of the national market leaders was demonstrated by the positions of the two largest manufacturers of architectural coatings, Sherwin Williams and Glidden (ICI) with market shares of 15.9% and 13.2%, respectively.¹⁸

The largest producers of architectural coatings also manufactured products which they categorized as industrial maintenance coatings. These products had similar characteristics, but often had been modified to offer application specific properties. Coatings used for chemical manufacturing facilities, for example, needed to provide greater corrosion resistance and durability than standard house paints. Similarly, paints used for corrosion protection on bridges needed to have specialized protective qualities. Sales of industrial coatings were primarily made directly to those responsible for facility maintenance for whom cost was a significant consideration.

18. "Prospects Improve for a Mature U.S. Market," Chemicalweek, October 31, 1990)

Distinctive Environmental Regulation in the United States

California led the regulation of paint emissions with the adoption in Los Angeles County of Rule 66 in 1966. The developers of this rule had determined, through the use of 8-hour smog chamber tests, that hydrocarbons had differing levels of photochemical reactivity and categorized substances into three classes based on their tendency to produce ozone. All facilities were compelled to remain below allowable emission levels for each category. In order to stay within the limits of regulations, paint users were required to maintain production at a level which kept emissions within compliance, adapt control equipment to collect and destroy paint emissions, or begin to use paints using innovative solvent systems which were described as California compliant.¹⁹

The first federal initiatives aimed at reducing VOC emissions resulted from the passage of the Clean Air Act Amendments of 1977. As required in the legislation, standards were established for acceptable levels of ambient ozone. States were compelled to develop plans for reaching compliance in non-attainment areas. The areas most out of compliance and thus requiring the most strict new standards were the LA Basin, the northern New Jersey/New York City region, Houston, and Chicago.

The 1977 Amendments required that the EPA provide guidance to the states in developing their implementation plans through the development of Control Technique Guidelines (CTGs). In addition, the EPA was responsible for developing new source performance standards (NSPS). These were rules governing the characteristics of new facilities regardless of whether or not they were in a non-attainment area. Control Technique guidelines were based on reasonably available control technologies while the NSPS outlined the best demonstrated technology (CTGs were less strict than the NSPSs).

Control Technique Guidelines provided emission reduction options for selected industry segments. Among the first were CTGs for the following industries: cans, coils, paper, fabrics, automobiles, light duty trucks, metal furniture, insulation magnetic wire, large appliances, miscellaneous metal parts, graphic arts, and flat wood paneling. Many of the guidelines were framed around a concept of allowable

19. California Air Resources Board, Daryl Bums, Telephone interview March 10, 1993

VOC content of the coating. For example, the CTG for automotive coatings put limits of VOC content at 1.2 lb/gallon excluding water for prime coats, 2.8 lb/gallon excluding water for guide coat and top coat, and 4.8 lb/gallon excluding water for paints used in final repair.

As a base CTGs were aimed at establishing methods for facilities to achieve an emission level equivalent to using existing coatings with a control system capturing 90% of emissions and achieving a destruction rate (efficiency of the system in reducing the materials to carbon dioxide and water) of 90%. However, some easing of the regulations was permitted to encourage the adoption of substitute coatings rather than end-of-pipe treatments. Negotiations with industry were conducted to establish requirements which could be met by existing coatings. The guidelines were also structured to allow manufacturers to use control devices if coatings containing higher VOC levels were chosen for performance reasons.²⁰

Although efforts were made to target large, growing industries with high contributions to ozone levels, CTGs were not issued for several areas with substantial VOC emissions. Notably, no CTG was issued for automobile refinishing primarily because of the recognition of the difficulty of achieving acceptable enforcement on tens of thousands of facilities. Similarly, no CTG was issued for architectural coatings because of the difficulty in enforcing a use regulation on a consumer product. In wood furniture coatings, no cost effective technology existed to reduce the very high levels of VOC content.

The 1990 Clean Air Act Amendments required that the EPA provide an additional eleven CTGs to the states. The Agency was responsible for identifying nine of these. Two were specified, aerospace coatings and ship building and repair. Aerospace manufacturers actually lobbied to have a CTG developed specifically for their industry. Given the unique demands of coatings used on a fuselage, aerospace manufacturers had been concerned that their coatings would be regulated according to the CTG for miscellaneous metal products.

20. U.S. Environmental Protection Agency, James Berry - Section Chief and David Salman - Industrial Engineer. Interview January 19, 1993

The 1990 amendments required that regulation of architectural coatings be accomplished through the development of a national rule. As with CTGs the focus of the national rule was to be on allowable levels of VOCs. The EPA included industry opinions in the rule making process by adopting a regulatory negotiation (reg-neg) process. The EPA provided information to manufacturers through this process, and industry was allowed to provide comments and proposals to the reg-neg for VOC levels with which they felt they could comply. Additionally, manufacturers were invited to "have seats at the negotiating table" where they could voice their recommendations for the developing regulations.

Sources of Competitive Advantage

Factor Conditions

Basic factor conditions were not a critical source of competitive advantage to the paint industry in the 1990s. Unlike the case in the early 1900s, the importance of factor conditions decreased significantly in the paint industry over the second half of the twentieth century. Originally, the industry required a ready source of such naturally occurring raw materials as linseed oil and turpentine. The availability of these materials had been a major factor in the early establishment of the industry in Louisville, Kentucky and Cleveland, Ohio.²¹ However, developments in organic chemistry resulted in a move away from naturally occurring materials throughout the middle part of this century.

With a limited reliance on natural production factors, the critical input to the U.S. paint industry was the knowledge of a specialized labor pool. The development of the industry relied on the creativity of individuals focused on providing new types of coatings through developments in resin and solvent chemistry. Following the many developments in organic chemistry occurring during the World War II, the ultimate raw materials of many paints were petroleum and coal distillates which had been modified and polymerized to enhance desired properties. As a result, in the major centers of U.S. paint manufacturing, Cleveland, Louisville, and Chicago, industry associations worked closely with academic

21. Schulenberg, Fred, "America's Great Coating Centers: Cleveland, Part I," American Paint and Coatings Journal, January 5, 1987, and Schulenberg, Fred, "America's Great Coatings Centers: Louisville, Part I," American Paint and Coatings Journal, May 19, 1986

programs to develop strong programs in Polymer science and coating technology.²² Notably programs at Case Western Reserve University, the University of Akron, and Kent State University (all near Cleveland) as well as the University Of Louisville had built strong ties with industry and frequently worked with the industry in technical development.

Domestic Demand Conditions

It has been noted above that paint and coatings markets must be segmented to understand the underlying demand conditions. In the (1990) \$4.9 billion U.S. architectural coatings market, buyers tended to make purchases infrequently. These customers made purchase decisions based on price, convenience of the purchase site, brand familiarity and ease of use of the product (particularly those that chose water-borne products). As a result, suppliers to this part of the market focused on cost controls and productivity improvements. Additionally, many manufacturers developed extensive distribution systems with company owned or franchised stores. Customers would seek advice in these stores concerning application methods, clean up requirements, and color matching. In larger companies such as Sherwin Williams, information would then be fed back to research and development areas to satisfy emerging customer needs.

In the OEM market and the special purpose market, however, highly sophisticated buyers reviewed a large variety of candidate coatings before selecting one which provided the required combination of properties. Paint manufacturers that were able to satisfy these changing needs on a continuing basis grew (and at times declined) with the industries they supported. The geographic grouping of the paint industry in Cleveland and Chicago owed its development to traditional partnering of OEM manufacturers of automobiles, carriages, and farm equipment with their coatings suppliers.

OEM buyers were, of course, concerned about price, but performance characteristics and ease of application were often more important than simple cost per gallon comparisons. This attitude was driven by the importance of the coating in marketing the product, particularly as compared to the overall selling

22. Schulenberg, Fred, "America's Great Coatings Centers: Cleveland, Part IV." American Paints and Coatings Journal, March 30, 1987 and Schulenberg, Fred, "America's Great Coatings Centers: Louisville, Part III," American Paints and Coatings Journal. June 16, 1986

price. For example, the total coating cost of a grand piano selling for \$10,000 would be only approximately \$25. However, the appearance of the instrument would dramatically affect its appeal to customers. A similar comparison was often made concerning the coating costs of automobiles. In this industry, several manufacturers pointed out that the "paint sold the car."

Process characteristics were a major concern of OEM buyers. The ability to improve transfer efficiency or reduce coating time could quickly offset higher costs of materials. Sophisticated OEM buyers looked at the total cost of coating and then made comparisons of the expected impact on the product's attractiveness to customers.

Because paint suppliers needed to be well informed on all aspects of the customers needs, strong relationships developed between the firms. Having made specialized developments, paint suppliers became aligned with particular segments of the market. Buyers would signal emerging needs and encourage new developments by the primary suppliers to the industry. In areas such as automobile and aerospace manufacturing, where the U.S. had led development at one time, coatings suppliers often led new developments later adopted by foreign manufacturers.

Related and Supporting Industries

The simplicity of paint manufacturing resulted in limited reliance on supporting industries for process equipment and services. However, modern paint companies depended on developments in polymer chemistry to provide innovative products to their customers. It is not surprising, then, that the strong positions of Germany, the Netherlands, and the United Kingdom identified above were supported by leading chemical industries. Although not leading, the U.S. chemical industry was strong in many areas and had particular success in polymer chemistry.

In each country with a competitive paint manufacturing industry, a cluster of industries supported by synthetic organic compound production was evident (see figure 1). These manufacturers provided the intermediary processes required to modify simple organic substances derived from naturally occurring sources (primarily coal and petroleum). Paint manufacturers developing new ways of satisfying buyers'

The Paints and Coatings Industry

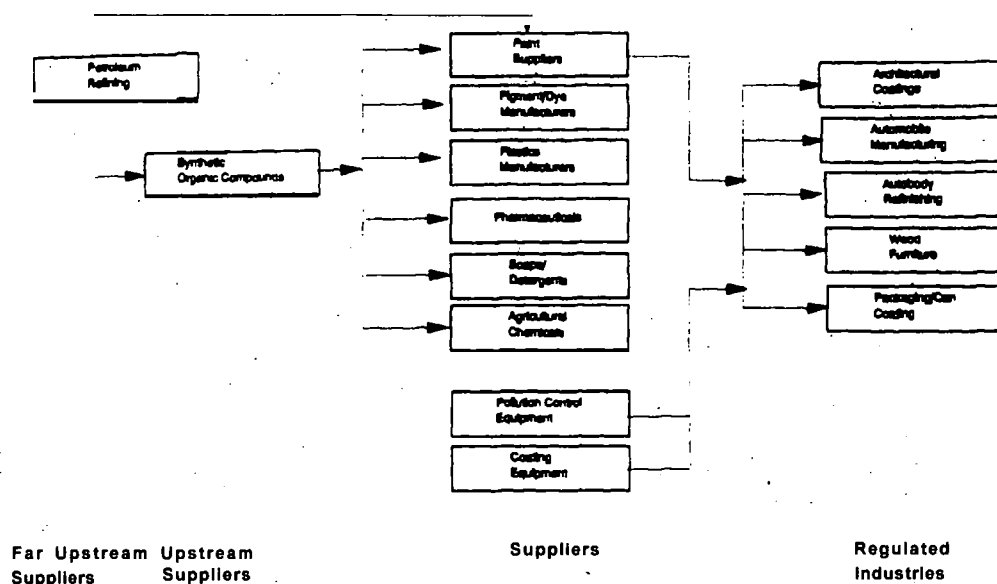


Figure 4: Industry cluster for paints and coatings manufacturing

demands relied on this industry to provide unique chemistries with previously unavailable combinations of properties. Typically, in countries where the synthetic organic compound industry was strong, other downstream industries besides paint were also strong. Other industries relying on innovative synthetic organic compound firms included plastics, pharmaceutical, soaps and detergents, and agricultural chemicals.

Strategy, Structure and Rivalry

In the U.S. the architectural coatings market was served by a large number of mostly small firms. In its early days the paint market was easy to enter, particularly in Chicago, Louisville, and Cleveland. The availability of raw materials, the relationship with customers, and the ready access to rail and canal distribution systems provide some explanation for why the coatings industry became important in these cities. Once the industry started, the low capital cost needed to enter the market encouraged many individuals to leave the firms where they received their training and begin their own operations. Firms

such as Peaslee-Gilbert (a strong early manufacturer and later a part of Devoe Raynolds) and Sherwin Williams developed reputations as the training ground for later entrepreneurs. Many of the new firms were started within a few miles of the firm where the founder had learned the business.

The intense rivalries among the small entrepreneurial firms yielded continued improvements in the areas most important to customers. Improvements in customer service and product quality and performance resulted. While each of the major paint manufacturers recognized that investments in research and innovation were of primary importance, they adopted different strategies. Sherwin-Williams, for example, invested in process technologies, such as new methods of milling pigments. The company developed a system that ground pigments fine enough to remain in suspension in the oil. This ensured a high quality of ready-mix paint. The Glidden Company researched better substitutes for paint media and solvents which led to the first nitrocellulose lacquers and other quick drying finishes. Continued emphasis on new materials led the company to introduce the first water-borne latex household paint in 1948. Reliance Universal, Inc. was an early leader in emphasizing research into custom formulations and applications for specific customers. The company then supported its investments into this strategy by adopting decentralized production, locating its plants close to customers.²³

Germany

Competitiveness Overview

In 1990, West German paint production was approximately 12% of world total at \$4.3 billion. This demonstrated annual growth of approximately 4% from 1985 production of \$3.6 billion (no data was available for unified Germany).²⁴ In 1990, West Germany had a commanding position with 25 % of world exports of paints and the largest positive trade balance of any country, \$800 million (tables 1 and 3).

23. Schulenberg, Fred, "America's Great Coatings Centers: Louisville, Part II." American Paints and Coatings Journal, May 26, 1986

24. "Restructuring Continues in Europe," Chemicalweek, October 31, 1990

Leading Firms

The major suppliers of paint in Germany were chemical companies which had forward integrated in a movement reported to have begun with the acquisition of Glasurit Werke Winklemann by BASF in 1965. In 1990, following further acquisition, BASF led manufacturers in German paint production with an estimated 25% share.²⁵ Hoechst (through its subsidiary Herberts), the British firm, ICI and the Dutch firm, Akro followed, each estimated market shares of more than 5%.²⁶

In 1985, BASF completed the largest investment in the U.S. paint industry ever undertaken. Reportedly to expand its position in automobile OEM and repair finishes, the company purchased the coatings operations of Inmont for a price of \$1 billion. In 1992, the U.S. operations of the company had revenue of \$975 million (including sales of printing inks and dyes).

Distinctive Environmental Regulations

Concerns with tropospheric ozone and thus emissions of VOCs were receiving growing attention in Europe in the early 1990s. As seen in Table 11, the level of VOC emissions was fairly well correlated with a nation's production. As a result, the leading producer nations took the lead in implementing regulations on the sources of VOCs.

On November 19, 1991, 23 countries signed a United Nations European Commission for Europe (ECE) protocol for reduction of VOCs. The aim of the agreement was for each country to achieve a 30% reduction in emissions by 2000. The definition of the base year was left to the signatory countries so that those such as Denmark or Switzerland where many controls were already in place were not unfairly penalized for their prior efforts. Additionally, less industrialized countries, Hungary, Bulgaria, Ukraine,

25 Information Research Limited, "A Profile of the West European Paint Industry," London, 1990

26. Information Research Limited, "A Profile of the West European Paint Industry," London, 1990

and Greece which had comparatively low ambient VOC levels agreed to "standstill" emissions at 1987 levels.²⁷

Although the signing of the protocol was the first step leading to regulations on paint composition and use, individual nations were expected to develop their own plans for reaching VOC reduction goals. By 1992, implementation systems were already seen to vary and decisions concerning when to address paint emissions versus automobile, petroleum marketing, chemical manufacturing and other areas differed among the signatory countries. At that time, the countries which were closest to direct regulation of coatings application were Germany, the UK, and the Netherlands (see below for discussions of specific regulatory approaches in the UK and the Netherlands).

In Germany, efforts to improve air quality originated with the 1974 Bundesimmissionschutzverordnung (BIMSchV), or Federal Immission Control Act. As in the use of CTGs in the U.S. Clean Air Act, the German legislation required implementation of the program in the Lander (states) according to recommendations in the Technical Instructions on Air Quality Control (TA Luft). The TA Luft was amended and updated periodically including changes occurring in 1986 and 1991. Until 1991, the primary impact on the paint industry was a requirement to receive formal approval for plants using more than 250 kg/hour of solvents. Manufacturers emitting higher levels were required to demonstrate equivalent reductions at other facilities. The impact on the paint industry was modest.

The 1991 amendments to TA Luft increased the stringency of requirements in the use of coatings. Regulations on coating processes in automotive manufacturing, for example, put limits on emissions of 60 grams of organic solvent emissions in the waste gas of the overall facility per square meter of car body

27 Dutch Ministry of Housing Physical Planning and Environment, "The ECE Protocol on VOC Emissions Elucidated," VOC Newsletter, February, 1992

surface covered.²⁸ As seen in table 12, this requirement was more strict than similar regulations in the U.K., but substantially higher than reported results of the best performing facilities in the U.S.

In other surface coating areas, the limits were based on allowable mass concentration of organic solvents in the waste gas (20 mg/m³ in spray booth areas, for example). Outside auditors using established guidelines performed yearly assessments to assure compliance. Switzerland, Austria, and Denmark traditionally used TA Luft as a model for their regulations, so similar rules on OEM coatings were anticipated to be implemented in these countries.

The Netherlands

Competitiveness Overview

Although the Netherlands only accounted for 3.9% of all world exports in 1990, the country was responsible for 11.0% of paint shipments (table 1). The Dutch balance of trade in the industry had risen from \$106 million in 1985 to \$268 million in 1990 (table 3). These values represented almost one third of the total production of the nation which was estimated in 1990 to be \$898 million.²⁹

Leading Firms

The Dutch paint industry was perhaps the most concentrated in all of Europe with Akzo controlling more than 40 % of the market followed by the Belgian owned Sigma Coatings with 25 % Smaller shares were supplied by Herberts of Germany and Kemira Color of Finland.³⁰

In 1989, Akzo acquired Reliance Universal of the U.S. for \$275 million. The acquisition was driven by an expressed desire to enter the large steady market for U.S. coatings. Reliance Universal with \$320 million in revenue had been held for several years by the Tyler Company, a holding company with very

28 The regulations go on to require "full use of the possibilities to further reduce the emissions by employing varnish systems which are poor in or free from solvents, highly effective coating procedures, air circulation procedures or by waste gas cleaning, particularly in the spraying areas."

29 "Restructuring Continues in Europe," Chemicalweek, October 31, 1990

30 information Research Limited, "A Profile of the West European Paint Industry," London, 1990

limited participation in the firm's operations. Tyler Company had acted as a white knight acquirer in a much earlier unfriendly takeover attempt of the firm.

Environmental Regulations

VOC reductions in the Netherlands were being targeted by a set of cooperative agreements established by KWS2000.³¹ Attempting to reduce emissions by 50% by 2000, partnerships which included industry, local government, and the federal government were formed to find solutions. Permit systems were to be used to monitor progress. The process was intended to be highly cooperative and extremely flexible in its ability to incorporate new information. In the following quote, representatives of Projectbureau KWS2000 described how the permit system was used to update facility performance once new information about technology was developed:

"In 1989, two projects were subsidized, demonstrating the use of water-borne and powder coatings for production of metal furniture. These projects were successful. Based on this, the Measure Group, supported by the Task Group Paint, set in a number of actions. First a list was compiled of all companies producing metal furniture. Second, the report was sent to these companies, and the corresponding authorities. The authorities were requested to take note of the content of these reports and to introduce the consequences into relevant permits. Third, the companies themselves were approached by an advisory institution, in order to inform the companies of this development, and to ascertain that they will indeed make the necessary arrangements. Lastly, the authorities will once again be approached some time in the future to find whether the measure has indeed been incorporated into the permits.³²

31. KWS2000's name is derived from the abbreviation for the Dutch word *koolwaterstoffen* meaning hydrocarbon and the goal of 50% reduction in emissions by the year 2000.

32. Projectbureau KWS2000, personal communication from Waldo Kaiser and Dominic Shrijer, March 12, 1993

In 1992, this program had had only a limited impact on the paint industry. However, as industrial firms exhausted the most easily targeted areas for reduction, coatings operations were beginning to be examined for potential opportunities.

United Kingdom

Competitiveness Overview

The British paint industry was characterized by slow growth throughout the late 1980s. Production was estimated at \$2.0 billion in 1985 and had grown less than 1% annually to \$2.1 billion in 1990.³³ In 1990, the UK was responsible for 10.9% of world exports of paint as compared to a 5.5% share of all exports and the paint industry possessed a positive balance of trade of almost \$230 million (tables 1-3).

Leading Firms

ICI, based in the UK, was the world's largest manufacturer of paints and coatings. In 1990, the firm had a 20% share of its home market.³⁴ Scandinavian firms Crown-Berger (owned by Casco-Nobel of Sweden) and Macpherson (owned by Kemira of Finland) followed with estimated 12.5% and 9.5% shares. Britain's other internationally strong producer Courtaulds held an 8.5% share of the home market.³⁵

ICI and Courtaulds had developed strong U.S. positions through acquisitions. In 1986, ICI had purchased the Cleveland firm Glidden, at that time the third largest coatings company in the U.S. The acquisition was consistent with ICI's explicit strategy of globalization. ICI acquired Glidden for \$580 million, when the company had pre-tax profits of \$60 million on sales of \$650 million.³⁶

33. "Restructuring Continues in Europe," Chemicalweek, October 31, 1990

34. Information Research Limited, "A Profile of the West European Paint Industry," London, 1990

35. Information Research Limited, "A Profile of the West European Paint Industry," London, 1990

36. Imperial Chemical Industries PLC, "Major Acquisition Makes ICI World Paints Leader, Company Press Release, August 15, 1986

Courtaulds had also expanded its presence in the U.S. coatings market through acquisitions. In 1987, the company purchased Porter Paints of the U.S. for \$140 million gaining a strong position in the midwest and southwest of the U.S. for architectural coatings. Porter Paints had been a privately held family business with sales in 1987 of \$120 million.³⁷ Courtaulds' U.S. OEM and industrial coatings positions were further strengthened through the purchase of Products Research and Chemical for \$260 million in 1989 and Desoto Industrial Coatings for \$135 million in 1990.³⁸ As a result of these transactions, Courtaulds ranked among the ten largest suppliers of coatings in the U.S. in the early 1990s.

Environmental Regulations

In the UK, passage of the 1990 Environmental Protection Act was expected to put demands on reducing VOC emissions from coating operations. Again, the primary federal responsibility was to provide assistance to local regulators and permit writers in methods of achieving emissions reductions. Guidance documents stipulating VOC content in industrial coatings were provided by Her Majesty's Inspectorate of Pollution. These documents outlined the "best available technology not exceeding excessive cost" (BATNEEC) for reducing emissions in industrial processes outlined in the Environmental Protection Act. Guidance documents were issued in a wide variety of areas affecting paints and coatings operations including vehicle manufacturing, wood furniture coating, refinishing of automobiles, and many others. In fact, the Environmental Protection Act may have covered more areas of industry than the regulations in any other country. However, as can be seen in tables 12 and 13, compliance requirements under the British regulations were less strict than those found in the rules of other countries.

"Rest of World" Markets

Large coatings manufacturers had entered the rapidly growing markets of Southeast Asia and Latin America by building new facilities. In the early 1990s, architectural coatings sales here were reported

37. Courtaulds Coatings Inc., "Porter Paint Co. Acquired by Courtaulds," Company Press Release, October 26, 1987.

38. U. S. Department of Commerce, "Foreign Direct Investment in the United States," 1990 Transactions

to have grown by more than 10% ,³⁹ making these regions significantly more attractive than home markets growing only at the rate of GDP. ICI, Sherwin Williams, Akzo, BASF, and Courtaulds had all made significant investments in these growing markets. Additionally, the two large Japanese manufacturers Nippon and Kansai had expanded markets into Southeast Asia. Although environmental regulations were limited in these markets, several manufacturers reported that production facilities in these areas were built to the most stringent environmental requirements of any of the geographies in which they had facilities.⁴⁰

39 "ICI Paints Chief Cites Growth in the New Hot Market: Asia," Chemical Week October 14, 1992

40 PPG Industries, Inc. Douglas B. Atkinson - Director Interview, February 25, 1993

EFFECTS OF REGULATION ON COMPETITIVE ADVANTAGE

Methods of Achieving Environmental Goals

As has been stated above, the first VOC paint regulations in the United States focused on the OEM segment of the market. Local rules, primarily in California, addressed manufacturers, but also put regulation on the content of architectural coatings. While compliance in architectural coatings was achieved almost exclusively through substitution of raw materials, manufacturing facilities have achieved lower VOC emissions in a variety of ways:

- * Substitution of new materials in the solvent/resin system
- * Development of coatings which did not require solvents
- * Adoption of application techniques with higher transfer efficiencies
- * Development of application devices which did not require solvents
- * Installation of control systems to capture and destroy or recover emissions

The following tables summarize how the adoption of these technologies affected the regulated groups and their suppliers. In cases where original equipment manufacturers were affected, the impending regulations were initially anticipated to drive substantial costs for abatement equipment. Many analyses of the impact of an environmental initiative stop at that point. However, as seen in these tables, projecting from the existing situation exclusively in the regulated industry overlooks the potential for innovation by that industry and, perhaps more importantly, by its suppliers.

The ability to offset the anticipated environmental costs for their customers led to strategic opportunities for a variety of coatings and equipment suppliers. Which firms benefited from these opportunities depended on their available resources, their ability to innovate, and the willingness of their customers to take risks in incorporating new technologies. Similar factors affected the opportunities in the market for architectural coatings; although here, regulators were potentially more influential in forcing customers to adopt new coatings.

Competitive Effects of Automobile Coatings Regulations on the Industry and Its Suppliers

Method	Automobile Paint Suppliers	Automobile Companies
High Solids Paint Systems	* Increased costs associated with development of new products	<ul style="list-style-type: none"> Expenditures for control equipment which reported to be as high as \$20-40 million in single facilities. Auto companies claimed environmental capital and operating costs of over \$40 per vehicle
		<ul style="list-style-type: none"> Diminished ability to achieve optimum surface finish
	* Share shift and licensing opportunities for innovative firms	
Waterborne Paint Systems	* Increased costs associated with development of new products	* Capital expenditures of approximately \$20 million per facility where sufficient space was available. Alternatively, similar additional costs for flash ovens in new paint lines
	* Share shift and licensing opportunities for innovative firms	Substantially improved appearance over high-solids paint systems
Powder or Radiation Cured Coatings Where Applicable		* Reduced coating costs through material savings

Competitive Effects of Wood Furniture Coatings Regulations on the Industry and Its Suppliers

Method	Equipment Suppliers	Coating Suppliers	Wood Furniture Companies
Adopt Control Technologies			<ul style="list-style-type: none"> Expenditures for abatement equipment
Supercritical CO ₂ Delivery Device	<ul style="list-style-type: none"> New market for suppliers of innovative equipment 	<ul style="list-style-type: none"> Share shift opportunities for innovative suppliers 	<ul style="list-style-type: none"> Equipment costs which were 20-33% of those anticipated for abatement equipment
			<ul style="list-style-type: none"> Lower coatings costs from reduced solvents
			<ul style="list-style-type: none"> Improved working conditions
			<ul style="list-style-type: none"> Improved surface appearance
Waterborne Coatings		<ul style="list-style-type: none"> Share shift opportunities for innovative suppliers 	

Competitive Effects of Architectural Coatings Regulations
on the Industry and Its Suppliers

Method	Architectural Coating Suppliers	Architectural Coating Users
Waterborne Paint Systems	I share shift opportunity for innovative suppliers	I Comparable cost to solvent-borne
		I Reduced odor and fumes from painting

Direct Effects on Product

OEM Markets for Innovative Products

Regulations on OEM coatings processes threatened to force substantial costs on manufacturers. Facility managers faced a choice between high costs for control equipment or adoption of innovative but developmental coatings which initially were not thought to provide the performance of previously used coatings. In response, suppliers undertook research efforts attempting to develop products which provided the required performance and could limit the need for control equipment. In a few large market segments which enjoyed competition from large technically sophisticated suppliers, dramatic changes in product technology occurred. However these investments were limited by traditional constraints on industrial innovations. Smaller suppliers simply did not possess the resources necessary for extensive technical efforts. The fragmented nature of the OEM coatings market, further worked against substantial research investment. Smaller market segments, although potentially large emitters of VOCs did not attract large investments because the potential rewards for the innovative suppliers were smaller. The ability of manufacturers to meet regulation with innovation was dependent on the structure of their own industry as well as that of their suppliers. The contrast between large concentrated industries and smaller fragmented markets can be seen in the following discussion of the automobile and the wood furniture markets as each of these industries faced increasing regulation on their releases of VOCs.

The market for transportation (automobile, truck, and other vehicle) coatings was the largest segment of the OEM market. In the U.S. alone, the 1990 sales for this segment were more than \$1.2 billion. In

addition, the market for autobody refinish coatings (categorized as special purpose because the product was not "original equipment") had sales of more than \$1.2 billion. These markets were supplied by large integrated Firms such as Dupont, BASF, and ICI. All of the major suppliers served this market as part of diversified chemical operations.

Painting an automobile was a complex process involving the application of several layers of coatings with baking processes in between. Each of these layers utilized differing formulations and application methods. As a result, concerns with solvent emissions varied depending on the step of the process. For example, very small amounts of VOCs were released in the application of the protective electrodeposition coat (E-coat) which was performed using a dip process in a water-borne coating.⁴¹

The application of the E-coat was followed by a primer surfacer and then a color coat. A great deal of attention had been focused on options for reducing the solvent content of the color coat. In the 1960s, two types of systems were used for color coats in the U.S. GM applied a monocoat lacquer while Ford and Chrysler employed low solids enamel systems.⁴² In response to a 1972 amendment to California's Rule 66, GM needed to change to a water-borne enamel system at its South Gate, California and Van Nuys, California assembly plants.

Unrelated to environmental concerns, the automobile industry faced a new challenge in the late 1970s. At that time, European imports were being marketed which had a clearly superior appearance than U.S. manufactured vehicles. European firms, notably BMW and Mercedes Benz, had introduced a new technology to their operations. Instead of searching for a single monocoat material which offered color, metallic, gloss, and protective properties, they used a two stage basecoat/clearcoat method. The basecoat could be formulated to control the metal components of the coating as well as incorporate high pigment loadings. The clearcoat could be engineered for gloss, "distinctness of image," and durability.

41. PPG Industries, William V. Wamick - Director Coatings and Resins Manufacturing, Interview, Pittsburgh, PA, February 25, 1993

42. Jamrog, Robert, "Automotive Water-Borne Coatings: Clean Air Legislation is Pushing Automakers Toward Water-Borne Basecoats," Products Finishing, October, 1993

The U.S. automobile industry shifted to basecoat/clearcoat technologies during the 1970s and early 1980s. However, regulations were such that any new plant would need to reduce emissions to the level achieved by those GM plants using water-borne enamels in California. GM, anticipating opening three new plants in 1980 and viewing the requirements based on water-borne enamels as inappropriate for plants where the two step basecoat/clearcoat was going to be applied, sued the EPA claiming the agency had built its regulation around obsolete technology. Further, GM positioned the discussion as an important competitive issue. They argued that if the U.S. auto makers were forced by the regulations to use the poorly performing enamels, they would surely lose additional market share to European and Japanese imports.

A compromise was reached in which manufacturers were granted innovative technology waivers to the New Source Performance Standards. The innovative technologies were based on achieving lower emissions while employing basecoat/clearcoat. Similarly, existing facilities were allowed more time to bring down emissions following the release of a Federal Register Notice from the Reagan Administration which encouraged extending the compliance deadlines.⁴³

After some disappointing attempts at using water-borne basecoats, the U.S. manufacturers began to adopt systems which were solvent-borne but higher in solids content. Increasingly strict regulations pushed the manufacturers to reduce solvent content to the point where performance trade-offs were again being made. With high solids, gloss and distinction of image were compromised.⁴⁴

European manufacturers watched U.S. developments closely. They anticipated growing regulations in their own markets (as occurred in Germany, Sweden, and the U.K.) and were anxious to avoid the performance trade-offs required by high solids basecoat/clearcoat systems. This led European automobile manufacturers and their coatings suppliers to work together to find an acceptable waterborne technology

43. U.S. Environmental Protection Agency, David Salman - Industrial Engineer, Interview October 5, 1993

44. Jamrog, Robert, "Automotive Water-Borne Coatings: Clean Air Legislation is Pushing Automakers Toward Water-borne Basecoats, " Products Finishing, October, 1993

which would match the appearance of low-solids solvent-borne basecoat/clearcoat systems. In 1986, Volvo began using a water-borne basecoat developed by ICI in its Gothenburg, Sweden facility. The coating used an aqueous microgel technology supplied by ICI which the company had begun to research in the late 1970s.⁴⁵

Water-borne basecoats of this type were quickly adopted at new installations by other manufacturers. At the same time, BASF was developing a different technology which proved successful for water-borne basecoats. By 1993, nine plants in Germany and two in other parts of Europe were using water-borne basecoat systems.

BASF and ICI began to transfer their technologies to the U.S. later in the decade. Although Imnont had researched water-borne systems prior to its acquisition by BASF, much of the technology used in the systems sold in North America relied on developments made in the European operations. DuPont and PPG, the only other two U.S. suppliers of basecoats licensed the ICI technology.

By 1993, industry leaders estimated that 20% of the world's automobile plants were using water-borne basecoats⁴⁶ In North America, four plants were using systems based on the ICI technology, two were using BASF, and one used multiple suppliers. Further, BASF was planning to provide water-borne basecoats to the \$1.3 billion U.S. autobody refinish market by 1993.⁴⁷ ICI, which had not previously supplied refinish paints in the U.S., had announced a similar entry into this market.⁴⁸

U.S. automobile manufacturers were quick to point to achievements in emissions reductions which occurred between the 1970s and the 1990s. In that time, average releases of VOCs per vehicle were

45. IDAC, Dr. J. Pearson, Managing Director, IDAC UK, Telephone Interview, August 23, 1993

46 "Environment Drives Automotives: Waterborne High-Solid Paints Spread," Chemicalweek. October 13, 1993

47 "Bodyshops Go Green," Polymers Paint Colour Journal

48. Wall, C., "Environmental Breakthrough for Refinish Paints," Polymers Paint Colour Journal

estimated to have been reduced from 15.5 pounds to 3.5 pounds, an 80% reduction.⁴⁹ They were just as quick to point out that these improvements were achieved at high cost in technology development, capital equipment, and possibly reduced sales resulting from lowered product attractiveness. Requirements outlined in the 1990 Clean Air Act Amendments put additional demands on the industry requiring even greater reductions, particularly in siting new or significantly modified facilities. Potential innovations which were being considered to meet these requirements included further adoption of water-borne base coat systems as well as utilization of powder coating systems for primer and clear coat operations.⁵⁰ If successful, these modifications were anticipated to bring the total release per vehicle to 1.5 pounds.

In contrast to the automobile companies, wood furniture manufacturers were often small firms with thin profit margins. The coatings market for this industry was much smaller with 1990 U.S. sales of \$340 million. Although this segment was fairly highly concentrated with four primary suppliers, its small size resulted in relatively low revenue for any one manufacturer. In southern California, rule 1136 required 93% reductions of VOC emissions from coating operations in this industry by 1996. Interim deadlines in 1989, 1990, and 1994 required substantial reductions. As the first deadlines approached, manufacturers were faced with a dilemma; few could afford control equipment and existing low solvent technologies were felt to be of substantially lower quality than higher solvent coatings. A study by the General Accounting Office in 1991 estimated that between 1 and 3% of these firms chose to relocate in Mexico in the years between 1988 and 1990.⁵¹ In addition, as many as 11% of other affected wood furniture manufacturers may have moved to other parts of the U.S. While many factors affected the

49. American Automobile Manufacturers Association, Interview, Bill King, May 27, 1993

50. United States Council for Automotive Research, "Plant Emissions Latest Big Three Research Target," Press Release, February 18, 1993

51. United States General Accounting Office, report on wood furniture manufacturer relocation to Mexico, April 24, 1991, B-243621, GAO/NSIAD-91-191

decision of these firms to move, 78% cited stringent air pollution control requirements as a significant factor in their decision (83% cited the high costs for workers' compensation insurance and wages).⁵²

Representatives of the South Coast Air Quality Management District reported in 1990 that the stringency of the regulations had been intended to prod furniture manufacturers into developing new low solvent coatings.⁵³ These regulators may not have considered that even the largest suppliers achieved revenues from this segment of less than \$100 million.

The requirements in southern California did highlight increasing concerns for wood furniture coatings. However, although supplying firms began intensive research efforts, the development of compliant coatings which had acceptable performance took several years and the process required cooperation with suppliers as well as customers (the wood furniture manufacturing industry).⁵⁴ By the early 1990s, significant improvements in the performance of water-borne coatings had been made in this segment and few companies were then moving operations.⁵⁵ However, for the estimated 1,000 - 7,000 workers who were displaced, the innovations came too late.⁵⁶

Development of No-Solvent Coatings

Achieving higher transfer efficiencies and lowering solvent content was not merely an environmental issue. Anything less than 100% transfer efficiency implies some level of wasted material. Overspray, the paint which is not deposited on the product, must be collected and disposed. Solvent is included in the paint merely to be released later. Obviously, elimination of solvent or improved transfer efficiencies could reduce cost. This fact led manufacturers to explore the potential of radiation cured and powder

52. United States General Accounting Office, report on wood furniture manufacturer relocation to Mexico, April 24, 1991, B-243621, GAO/NSIAD-91-191

53. Kraul, Chris, "A Warmer Climate for Furniture Makers," The Los Angeles Times, May 14, 1990

54. Lilly Industries, Inc., 1991 Annual Report, "Research and Development: Our Foundation for the Future"

55. Lilly Industries Inc., Bob Bailey - Vice President of Marketing, Telephone Interview, February 11, 1993

56. United States General Accounting Office, report on wood furniture manufacturer relocation to Mexico, April 24, 1991, B-243621, GAO/NSIAD-91-191

coatings. These materials offered the possibility of solvent free coating application with almost 100% transfer efficiency.

Radiation cured coatings used low molecular weight monomers which reacted to form a film when exposed to UV light or electron beams. Powder coatings were typically applied through an electrostatic deposition process and then exposed to heat. When the coating reached its melting point a thin resilient film was formed. The prospect of increasing environmental regulations limiting VOC emissions spurred growing interest in both radiation cured and powder coatings in the early 1990s. Expansion of these markets was anticipated by most paint market analysts.⁵⁷ In 1990, however, radiation cured coatings and powder coatings each constituted only about 2% of the total paint market.⁵⁸

The primary limitation on radiation and powder coatings was the difficulty in achieving acceptable finishes when applying the material to non-uniform surfaces. Radiation coatings could only be applied to flat surfaces so applications were limited to such areas as flat wood paneling and printing applications. Using electrostatic processes, powder coatings could be applied to more varied surfaces. However, appearance problems were still being overcome in the early 1990s. Although increasing advances were expanding the markets for these coatings into such areas as automotive finishes and metal furniture paints, the largest markets for powder coatings remained in areas of simple geometries. In 1992, appliance coatings accounted for 21 % of powder coating markets and coatings for simple automotive parts (such as underbodies and wheels) made up 15 %.⁵⁹

OEM Markets for Innovative Equipment

Some regulations in California addressed transfer efficiency as well as solvent content of the coating. Transfer efficiency was a measure of the ratio of the amount of coating deposited on the substrate to the

57 U. S. Department of Commerce, U. S. Industrial Outlook, 1993, "Paints and Coatings," p. 11-8 through 11-9

58. U. S. Department of Commerce, Current Industrial Reports, Paints and Allied Products, 1990

59. Powder Coatings Institute, "Powder Coatings - Markets and Applications," Gregory J. Bocchi, Executive Director, 1993

total amount of coating used in the painting process. Using a low VOC paint in a process with poor transfer efficiency would provide little benefit overall in reducing VOC emissions. As a result, in those areas where manufacturers had options in application devices, tables were developed which applied a transfer efficiency rating to each device. Higher VOC content was permitted with higher transfer efficiency.⁶⁰ Rules 1136 and 1151, promulgated by the South Coast Air Quality Management Board (SCAQMB), attempted to achieve a minimum of 65% transfer efficiency. The rules stipulated that if spray guns were used they had to have a maximum nozzle pressure of 10 psig (pounds per square inch, gauge). Spray equipment which complied with this rule was termed High Volume/Low Pressure, HVLP, and used high speed turbines rather than compressed air to atomize the coating.

Industry challenged the equipment specifications of rules 1136 and 1151. Manufacturers claimed that many factors affected transfer efficiency and that spray equipment was potentially less important than other issues.⁶¹ Further, they suggested that use of HVLP equipment would increase spray time and thus increase costs of manufacturing operations.

A comprehensive study of spray painting systems used in wood furniture manufacturing concurred with manufacturers' worries about the equipment. In this study, four types of coatings were used in six types of spray equipment. An expert and a novice painter coated doors and window frames to determine the influence of different factors in reducing VOC emissions. The researchers concluded that using water-borne coatings and having painters become more proficient were the most effective methods of reducing VOC emissions. Surprisingly, in about half of the cases, using HVLP equipment resulted in lower transfer efficiency than using conventional airspray systems (and required more time). Air assisted HVLP equipment provided a desirable combination of reduced spray time and lowered VOC emissions.⁶²

60. U.S. Environmental Protection Agency, James Berry - Section Chief and David Salman - Industrial Engineer, Interview January 19, 1993

61. Schrantz, Joe and Bailey, Jane, "Under the Gun to Conform in California," Industrial Finishing, June 1989

62. Snowden-Swan, Lesley, "Transfer Efficiency and VOC Emissions of Spray Gun and Coating Technologies in Wood Finishing," Battelle Pacific Northwest Laboratories, Pacific Northwest Pollution Prevention Research Center, November, 1992

Improving transfer efficiency provides a clear example where better environmental performance could be coupled with attractive economics. However, the study discussed above suggested that the methods required by SCAQMB were not necessarily the best means of achieving these goals. These results suggest that regulators must be cautious in being overly prescriptive in identifying means of achieving environmental improvement even when those means should provide economic advantages. Subtle differences in facilities, in products, and - as in this case - operator skill can substantially influence anticipated outcomes.

One of the most innovative approaches to reducing VOC emissions from paint application was the Unicarb system developed by Union Carbide in 1989. Rather than look to other types of liquids to replace existing solvents, the company developed a system which took advantage of the solvent-like properties of carbon dioxide under high pressure. Termed "supercritical," the highly pressured carbon dioxide replaced the "cutting solvent" which was used to carry the resin and pigment through the application device. It volatilized prior to deposition on the product, similar to a cutting solvent. Coalescing solvents which remained in the system ensured a smooth layer and uniform film thickness.⁶³

The Unicarb system was initially developed in response to environmental concerns, but the earliest applications of the technology were in locations where VOC regulations were not particularly strict.⁶⁴ The company suggested that additional benefits spurred manufacturers to switch to the Unicarb system. Some of the advantages claimed by the company included:⁶⁵

- * Improvement in working conditions because carbon dioxide is odorless
- * Improvement in safety because carbon dioxide is not flammable
- * Superior coating performance through the use of higher molecular weight resins

63. Union Carbide Chemicals and Plastics Company Inc., "Unicarb System for Spray Coating: A major Advance in VOC-Reduction Technology," Company Promotional Literature

64. Union Carbide Chemicals and Plastics Company Inc., Dr. Dave Buzby - Development Scientist, Telephone Interview, March 8, 1993

65. Union Carbide Chemicals and Plastics Company Inc., "Unicarb System for Spray Coating: A Major Advance in VOC-Reduction Technology," Company Promotional Literature

- * A more uniform surface than other low VOC systems
- * Low capital expenditure compliance option

The company claimed that the cost of removing VOCs using the Unicarb system ranged from one-third to one-fifth that of using carbon absorption or incineration systems.⁶⁶ Union Carbide chose to market neither coatings nor application equipment. Instead, the technology was being licensed to several firms specializing in each of these areas.

Architectural Coatings Markets for Innovative Products

In architectural coatings, the trend toward lower solvent products had continued since the first introduction of water-borne coatings by Glidden in 1948.⁶⁷ Many of the advantages driving this trend were summarized in an industry response to the EPA during negotiations over the adoption of architectural coatings rules in 1993:

"As with all highly competitive markets, reducing product costs and introducing technological innovation are among the chief means by which a company can increase its market share. This fact has been largely responsible for the shift from solvent-borne products -- a shift that has both reduced manufacturers' cost by reducing the solvent content of products and responded to consumers' demand for products that have less odor and are easier to clean up."⁶⁸

However, the same document went on to identify five deficiencies in water-borne paints as compared to solvent-borne systems:

66. "Supercritical CO₂ as a Solvent: Update on Union Carbide's Process," Modern Paint and Coatings, June 1990

67. Yerak, Rebecca, "No-smell Coating: New Glidden Paint Safe for Environment," The Plain Dealer, Cleveland, Ohio, July 21, 1992

68. "Responses: Questions and Issues Raised by State, Environmental, and EPA Members of the AJM Reg-Neg Committee Concerning the Industry Caucus Proposal of January 6, 1993," Response Submitted to the Full Reg-Neg Committee on February 11, 1993

- * Water-borne products were more sensitive to surface conditions

- Water-borne coatings could be more difficult to apply

- Water-borne paints dried quickly but "cured" slowly

- * Water-borne paints did not cure at lower temperatures

- * Water-borne products generally formed a softer film than solvent-borne coatings

Thus, the message from producers of architectural coatings was in support of regulations which had an accelerating effect on existing market trends. However, flexibility was desired to allow continued production of coatings for applications with requirements closely matched to the characteristics of high solvent coatings. Unfortunately, regulators could never be sure that specific coatings would only be used for the narrow applications for which they were intended. Therefore, regulators tended to demand lower solvent levels in all coatings intended for consumer purchase.

Limitations to Innovation

Clearly, the regulations affecting VOC emissions showed a variety of approaches to innovation. However, in a series of legal challenges (primarily in California) and responses to pending regulation, industry raised some concerns about the ability to innovate within the structure of the regulations. The primary issues which were raised follow:

I An industry sponsored group in California won a lawsuit against pending architectural coatings regulations making, among other claims, the assertion that the rules would encourage the use of inferior coatings. It was argued that consumers would be forced to use more paint, or repaint more frequently, and therefore, VOC emissions could be exacerbated by the regulations.

I Again primarily in California, manufacturers complained that tests for measuring transfer efficiency were poorly designed. It was asserted that lower VOC coatings used in application systems with lower transfer efficiency would continue to yield high emissions.

I In the U.S. none of the regulations rewarded the advantages of thinner coatings. Because thinner coatings required less paint to cover a surface, less VOCs would be released in using a thinner, rather than a thicker coating. Although not addressed in the regulations, the thickness of the coating could significantly affect the amount of paint used and thus the VOC emissions resulting from coating a surface. Automotive coatings, for example, ranged for 2.4 to 3.8 mils (a 58% difference).

I Some industry groups claimed that focusing regulations only on coatings operations did not allow firms to be in compliance by achieving equivalent reductions in emissions in other areas of operations. At times industry intentions appear to have been more to be provocative than practical. For example, the South Coast Finishers and Fabricators Association (SCFFA) recommended to the South Coast Air Quality Management District that emissions targets set for wood furniture manufacturers could be met more cheaply by adopting car pooling and staggered shifts (so travel would occur at less congested times). It was argued that reducing the emissions from employees' cars would more than achieve the goals set for the coatings

Traditionally, water-borne architectural coatings had been priced at or below the price of solvent-borne systems.⁶⁹ However, manufacturers have reported that raw material costs for totally new paint technology may initially have been 20-30% higher.⁷⁰ The confusion on this issue was not cleared up even after extensive study by the State of California Air Resources Board. In July of 1989, the Technical Review Group of the Architectural Coatings Committee concluded, "the economic impact to consumers from reformulating coatings can be either positive or negative and is difficult to estimate."⁷¹

The primary cost concern to industry had not been the change in raw material prices. In the early 1990s, the cost of developing new formulations was the most important concern for many firms. At a minimum, the development of a new coating required the dedication of two researchers with access to necessary laboratory and pilot production facilities.⁷² Development typically took two to four years with the latter stages requiring long-term performance testing.⁷³ Particularly when changing to water-borne systems, production facilities could be required to be modified to handle new materials in the formulations.⁷⁴ Clearly then, the development of a new coating could reach costs in the hundreds of thousands of dollars.

As has been described, the structure of the architectural coatings industry was very different than that of OEM coatings suppliers. In 1990, the three largest manufacturers accounted for 36.5% of the market. Meanwhile, hundreds of small manufacturers, with little or no development capabilities were producing

69 "Responses: Questions and Issues Raised by State, Environmental, and EPA Members of the AIM Reg-Neg Committee Concerning the Industry Caucus Proposal of January 6, 1993," Response Submitted to the Full Reg-Neg Committee on February 11, 1993

70. Courtaulds Coatings, Stanley Hope - Manufacturing & Environmental Manager, Interview, April 13, 1993 and Glidden Co., Jim Sainsbury - Manager Products Regulation, Interview, February 18, 1993

71. California Air Resources Board Stationary Source Division, "ARB-CAPCOA Suggested Control Measure for Architectural Coating: Technical Support Document," July 1989, p. 22

72. Courtaulds Coatings, Stanley Hope - Manufacturing & Environmental Manager, Interview, April 13, 1993 and Glidden Co., Jim Sainsbury - Manager Products Regulation, Interview, February 18, 1993

73. Glidden Co., Jim Sainsbury - Manager Products Regulation, Interview, February 18, 1993

74. Courtaulds Coatings, James K. Chapman - Vice President Manufacturing & Distribution, Interview, April 13, 1993

small quantities of material. Adopting highly restrictive or technology forcing regulations would likely provide a strategic advantage to the largest firms who could spread the cost of development over the greatest volume. In fact, some of the largest producers had already dedicated large investments to providing paints with reduced VOC emissions.

In 1992 Glidden introduced the first architectural coating to employ no organic solvents at all. Using an innovative resin system developed by Rohm & Haas Chemical Co., the company was able to eliminate even the coalescing solvents which were normally needed to assure a smooth surface finish.⁷⁵ The company highlighted the additional benefits of low odor and ease of clean up, but the primary motivation for its development was the recognized market for environmentally friendly products.⁷⁶ However, by having no VOCs, the product formulation was well beyond the requirements of even the most stringent California regulations. As has been noted earlier, Glidden became part of the ICI paints World Group in 1986. The management of this organization had concluded that long term regulatory trends would reward those companies which developed technical expertise in areas where negative environmental impacts of products could be reduced.⁷⁷

When Glidden set out to develop a solvent free product, the company decided that to be successful, the paint would have to achieve the desired environmental benefits with no reduction in performance. A particular difficulty was to assure acceptable hardness of the coating (this was important for trim areas such as windows and doorways). The solvent which was part of existing water-borne coatings was used as a coalescing agent promoting a harder paint surface. Achieving the required hardness in a solvent free coating required using a 100% acrylic resin system. This resulted in raw material costs substantially higher than those for many other Glidden products. Pricing was comparably higher. One source

75. Yerak, Rebecca, "No-smell Coating: New Glidden Paint Safe for Environment," The Plain Dealer, Cleveland, Ohio, July 21, 1992

76. The Glidden Company, "Glidden to Remove Petroleum-Based Solvents From Architectural Paints: First Solvent-Free Traditional Paint to Arrive in June," Company Press Release, May 28, 1992

77. Glidden Co., David Maurer - Product Planning Manager, Telephone Interview, August 27, 1993

reported pricing 50% higher for the solvent free paints than for traditional latex brands.⁷⁸ Within Glidden's existing channels of distribution, this price difference appeared dramatic. However, the company pointed out that if a comparison was made to other paints with high acrylic content the pricing was more similar.⁷⁹ Most of these were sold through paint stores where customers were more likely to make purchase decisions based on subtle characteristics of performance. Glidden, on the other hand, had marketed its coatings through large retailers and home improvement stores where price was more important.

Glidden marketed the acrylic resin water-based product in the U.S and Canada and anticipated entry into Australia. In the U.K., ICI used a different formulation for its VOC-free paint. British customers routinely used different paints for trim than they used for walls. Trim paints were formulated from alkyd resins which provided a very hard glossy surface. The paints used on the larger wall areas (flat paints) could be softer and were mostly latex type. Without the need for high hardness, ICI had developed a different type of solvent free paint which did not require coalescing solvents. The differing approaches demonstrates that in some cases, even with similar environmental requirements, different market characteristics lead to different innovations.

Indirect Effects on Pollution Control Industries

Regulations aimed at reducing VOC emission from coatings focused on achieving reductions equivalent to employing control devices with high levels of efficiency. Although this could require a significant capital expenditure, some manufacturers chose to modify production facilities rather than substitute new coatings. In coil coating lines (products used for metal building siding and other applications), manufacturers used medium and high solids coatings with incinerators on the ovens to burn the solvents⁸⁰

78. Yerak, Rebecca, "No-smell Coating: New Glidden Paint Safe for Environment," The Plain Dealer, Cleveland, Ohio, July 21, 1992

79. Glidden Co., David Maurer - Product Planning Manager, Telephone Interview, August 27, 1993

80. Lilly Industries Inc., Bob Bailey - Vice President of Marketing, Telephone Interview, February 11, 1993

CONCLUSIONS

Innovation is an important part of improving the quality of the environment while maintaining a strong industrial base. As demonstrated by paint suppliers, firms will dedicate large resources to these innovations when the regulations are structured to allow new approaches to compliance and the management of the firm feels the market being created is sufficiently large to provide returns on the resources dedicated to achieving new developments.

1) If regulations are likely to be met by supplier innovations, the size and resource availability of those firms will significantly affect their response to new requirements on their products.

The actions taken by architectural coatings manufacturers demonstrated the effect of varying resources on the response of industry to new regulations. For firms affected by regulation, the availability of resources may not be equivalent. Large firms may be able to quickly respond to regulations with innovative solutions which satisfy all product performance needs including regulatory compliance. At the same time, smaller firms, unable to match the development budgets of their larger rivals, may have no option but to resist and delay the regulations as much as possible.

This conflict could be seen in the early response to regulations on architectural coatings. In 1993 there were hundreds of manufacturers of architectural coatings. The top five supplied more than 45% of the market and each had sales of more than \$180 million, but the typical architectural coatings firm had revenues of less than \$5 million. In 1993, the regulatory negotiation was on-going concerning a national rule for VOC reduction in architectural coatings. Regulations which demanded rapid compliance or significant changes in product formulations would be expected to provide competitive advantages to the larger manufacturers with the resources to devote to research and development of new coatings. Smaller firms would not be able to keep up. As was already evident, as regulations began to take effect in California, large firms had begun to innovate with lower VOC formulations - even achieving a no VOC system - while many smaller firms had resisted regulation through litigation. Without some form of intervention, these firms could have become the losers in the trade-off between achieving regional

environmental goals and maintaining the existing characteristics of the industry's competitiveness. On the other hand, protecting small firms by adopting less rigorous standards or allowing longer implementation periods would have required accepting reduced environmental benefits.

2) Supplying firms will only respond to regulations with innovations in those markets which are large enough to justify their dedication of research resources.

The response of the paint industry in different OEM markets provides insights to the importance of the size of the market for innovative approaches to compliance. OEM manufacturers made significant progress in reducing the level of VOC emissions resulting from their coating operations between 1986 and 1991. The 15 % reduction in these emissions which resulted was achieved through the use of a variety of methods including material substitution, equipment changes, and adoption of control devices. In each of these areas, the products and equipment needed to achieve lowered emissions were developed by supplying industries to the ultimate manufacturer. For the upstream industries, the promulgation of regulations either created or significantly altered the industry's market. In every case, the upstream innovations provided additional options for lowering VOC emissions in coating operations. As a result, many manufacturers were able to reach (and at times exceed) compliance at costs significantly lower than would have been possible had regulations exclusively demanded the use of pollution control equipment.

As it became clear that automotive manufacturers would progressively move toward water-borne coatings, the large size of this market provided satisfactory justification for suppliers to research and improve these products. On the other hand, when only California regulated wood furniture manufacturers, the small size of the market and the technical difficulties encountered delayed manufacturers from achieving compliant coatings. Lacking innovative, lower cost solutions, some manufacturers found it impossible to compete with unregulated manufacturers and moved operations. Even as national regulations were being developed in 1993, it was unclear whether manufacturers would be able to supply all wood furniture markets with water-borne coatings which performed comparably to solvent-borne systems.

3) Those companies which target long term trends will be best positioned to benefit when regulations are adopted.

When U.S. automobile manufacturers were first regulated for VOC emissions, they responded by adopting the best then available option, high solids coatings. At that time, no suitable water-borne base coat was available. However, ICI had conducted more than a decade of research in hopes of developing a water-borne coating which could match the performance characteristics of solvent-borne base coats. Although ICI's customers were not likely to be regulated until the mid to late 1990s the company was able to achieve benefits from their research by licensing U.S. suppliers to use their technology. Additionally, the applicability of the technology to the larger automobile refinishing market, facilitated the company's entry into a market in the U.S. where it had previously not participated.

The characteristics of innovations in the paint industry have implications to any other regulated area. Here, as in many other areas, the innovations have not occurred within the regulated industry itself. Instead, new approaches were developed by suppliers at least one step up the value chain. In the case of new resin systems, the new developments were several steps upstream. These upstream industries must choose how to dedicate scarce resources. They will dedicate these resources to methods of lower cost environmental compliance when the regulations are structured to allow creative methods, the market for innovations is large relative to the required development investment, firms possess the needed resources, and the decision makers in the regulated area are receptive to new approaches of achieving compliance.

TABLE 1
World Export Share Development
Paints and Varnish

Country	1980	1985	1990
West Germany	23.1%	23.3%	24.6%
United Kingdom	11.9%	10.5%	10.1%
Netherlands	11.1%	10.6%	10.7%
United States	9.1%	9.3%	9.2%
France	7.5%	7.4%	7.1%
Belgium	4.9%	5.3%	5.3%
Japan	4.1%	6.2%	4.1%
Italy	4.6%		5.0%
Finland	2.1%	1.5%	1.6%
Switzerland	1.7%	2.0%	2.2%

Source: UN Trade Statistics Yearbook 1990

TABLE 2
World Import Share Development
Paints and Varnishes

Country	1980	1985	1990
West German	7.8%	7.2%	9.3%
United Kingdom	4.1%	5.1%	6.0%
Netherlands	6.0%	6.0%	5.8%
United States	1.1%	2.7%	3.0%
France	9.6%	8.4%	9.5%
Belgium	5.8%	4.9%	6.2%
Japan	2.1%	2.0%	1.7%
Italy	4.7%	4.8%	5.4%
Finland	1.4%	1.2%	1.4%
Switzerland	3.3%	3.1%	3.1%

Source: UN Trade Statistics Yearbook, 1990

TABLE 3
Trade Balance Development
Paints and Varnishes
(thousands)

Country	1980	1985	1990
West Germany	\$347,768	\$353,753	\$802,815
United Kingdom	\$176,533	\$120,377	\$229,077
Netherlands	\$127,169	\$106,361	\$267,967
United States	\$173,315	\$151,23	\$317,536
France	(\$14,668)	(\$5,260)	(\$65,685)
Belgium	\$283	\$16,115	(\$543)
Japan	\$49,100	\$90,492	\$154,060
Italy	\$11,881	\$2,965	\$10,323
Finland	\$17,97	\$9,029	\$16,268
Switzerland	(\$25,412)	(\$17,663)	(\$25,609)

Source: UN Trade Statistics Yearbook 1990

TABLE 4
World Export Share Development
All Pigments and Paints

	1980	1985	1990
West Germany	25.6%	24.7%	24.0%
United Kingdom	13.2%	11.5%	10.9%
Netherlands	9.4%	9.0%	8.0%
United States	7.0%	7.3%	10.1%
France	8.5%	8.9%	7.3%
Belgium	6.6%	6.5%	7.0%
Japan	4.6%	6.8%	6.0%
Italy	4.6%	4.4%	4.1%
Finland	2.6%	2.7%	2.4%
Switzerland	2.7%	3%	2.1%

Source: UN Trade Statistic Yearbook 1990

TABLE 5
World Import Share Development
All Pigments and Paints

Country	1980	1985	1990
West Germany	8.7%	8.3%	9.7%
United Kingdom	3.9%	5.0%	6.0%
Netherlands	5.7%	5.5%	5.4%
United States	2.5%	6.7%	5.7%
France	9.4%	7.9%	9.2%
Belgium	5.1%	4.2%	5.2%
Japan	2.4%	3.1%	2.8%
Italy	5.3%	5.1%	6.1%
Finland	1.2%	1.0%	1.1%
Switzerland	3.5%	3.2%	3.1%

Source: UN Trade Statistic Yearbook, 1990

TABLE 6
Trade Balance Development
All Pigments and Paints
(thousands)

Country	1980	1985	1990
West Germany	\$820,153	\$775,732	\$1,702,246
United Kingdom	\$446,536	\$308,755	\$596,105
Netherlands	\$196,671	\$168,586	\$302,945
United States	\$215,683	\$38,210	\$572,1
France	\$ 6	\$60,53	(\$156,331)
Belgium	\$93,683	\$113,392	\$244,462
Japan	\$112,336	\$178,9	\$388,461
Italy	(\$5,267)	623,449)	(\$190,595)
Finland	\$70,195	\$81,693	\$150,749
Switzerland	(\$19,309)	(\$4715	\$83,305

Source: UN Trade Statistic Yearbook, 1990

TABLE 7
U.S. Total Quantity and Value of Shipments of Paint and Allied Products

Category	1988 Value(million)	1989 Value (million)	1990 Value (million)
Architectural Coatings	\$ 4 4 2 6	4,525.3	\$4,913.6
Product Coating OEM	\$4,104.5	\$4,220.1	\$4,032.3
Special Purpose Coating	\$2251.8	\$2,493.5	\$2,781.5
Miscellaneous Allied Products	\$1052.3	\$1092.7	\$1,170.7
Total	\$11,835.4	\$12,331.6	\$12,898.4

Source: U.S.. Department of Commerce, Current Industrial Reports, Paint and Allied Products, 1991

TABLE 8
European Paints and Coatings Production
(millions)

Country	1985	1990
West Germany	\$1,583	\$4,312
France	\$2,111	\$2,585
United Kingdom	\$2,028	\$2,111
Italy	\$1,585	\$1,993
Netherlands	\$735	\$898
Spain	\$640	\$751
Belgium	\$439	\$544
Sweden	\$465	\$504
Switzerland	\$345	\$439
Denmark	\$379	\$417

Source: Chemicalweek, October 31, 1990

TABLE 9
Leading U.S. Architectural Coatings Manufacturers
(millions)

Company	1989 U.S. Sales
Sherwin-Williams	\$750
Glidden	\$620
Benjamin Moore	\$350
PPG Industries	\$303
Desoto	\$180
Kelly Moore	\$175
Valspar	\$170
Crow Group	\$160
Pratt & Lambert	\$140
Porter Paint	\$105

Source: Chemicalweek October 31, 1990

TABLE 10
Volatile Organic Compound Emissions of Selected Industrialized Countries

Country	GDP (\$ billion)	Population (million)	VOC (millionton)	VOC/GDP lb/SK	VOC per capita lb/capita
U.S.A	5,673	252.5	16.9	6.57	148
Austria	164	7.8	0.5	6.72	141
Sweden	230	8.5	0.4	4.22	114
France	1,032	57	2.77	5.92	107
U.K.	913	57.6	2.7	6.52	103
West Germany	1,234	63.7	2.6	4.64	90
Netherlands	249.1	15	0.5	4.16	69
Italy	969	57.8	1.53	3.48	58

Sources: 'Handbook of International Economic Statistics, 1992; U.S. EPA 'National Air Pollution Emission Estimates, 1900-1991, October 1992,' U.S. Department of Commerce. 'Western Europe Office, Country Profiles; VOC Newsletter, 8/92, Projectbureau KWS 2000. The Hague. The Netherlands: Statistics Sweden 'The Swedish Environment, 1991; Centre Interprofessionnel Technique D'Etudes de la Pollution Atmospherique (CITEPA). 'Emissions De COV; Reglementations Francaise Et Europeenne, Techniques De Reduction' 1992; U.K. Department Environment, Personal Communication from Norman Horrocks, 'Reducing Emission of VOCs: A U.K. Strategy.'; Federal Ministry for the Environment, "Environmental Protection in Germany," June 1992; Project Group Hydrocarbons 2000. 'Control Strategy for Emissions of Volatile organ Compounds Project KWS 2000. Department of Air Pollution, Ministerio Del Ambiente, Personal Communication, M. Gusparini M. Rizz

TABLE 11
Comparison of Regulations: Automotive Manufacturing

Allowable emissions per vehicle (assuming 110 square meters of surface area per vehicle and using performance results reported by American Automobile Manufacturers Association for U.S. values)

	United States	Germany	United Kingdom
Emissions (grams)	1,590	3.850	6,600
Emissions (pounds)	3.5	8.5	14.5

TABLE 12
Comparison of Regulations: Wood Furniture Manufacturing

Allowable solvent content in coating materials

	Southern California	United Kingdom
Clear Topcoats	275 g/l	400-435 g
Pigmented Coatings	275 g/l	525 g/l

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July, 2002

Chromium as a Paint Ingredient

Q. I am trying to find out whether chromium is (or has been used historically) as an ingredient/constituent in paint. The situation that we have is as follows: we have an old piece of equipment (dates back to the 1960's-early 1970's) that is made of metal and was painted. We are looking to dispose of this old machine and we had some paint chips tested (TCLP) and learned that chromium was present. What we are trying to figure out in order to properly dispose of this is whether the paint may have contained chromium as an ingredient or whether the chromium may have "leached" from the metal (equipment itself). We have seen other interesting ingredients used in making paint (including various other metals and even PCB's) and thought that chromium might also be a possibility. I would welcome any information that you may have on this issue.

A. Chromate containing (hexavalent chromium) pigments are still used in corrosion inhibitive primers, and it is quite possible that some of the chromium that you are seeing comes from the primer. Also, prior to the 1980s, many of the reds, yellow, oranges and derivatives of these colors, such as some greens, had a high lead-chromate content. In the 1980s due to OSHA regulations, many of the colored paints, as listed above, were reformulated so as to exclude lead and chromate ingredients.

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Solvents in Paints & Coatings



Making paint 'paintable' and fast drying...

Solvents are used in paint manufacture to dissolve the different compounds used in the paint formulation such as colour and binder, making the paint the correct consistency for application. Once the paint has been applied the solvent evaporates, allowing the resin and pigment to produce a film of paint and to dry rapidly. Without solvents it would be impossible to produce durable, decorative and, in particular, glossy paints for use both indoors and outdoors to withstand all conditions.

Fast drying saves energy...

Solvents evaporate readily and thus reduce energy consumption and minimise costs. Solvent based systems dry up to 10 times faster at room temperature than low solvent alternatives, keeping production rates up,

costs down and minimising energy consumption.

Standing up to harsh environments...

A manufacturer can use different solvents to produce coatings with very diverse characteristics. For example, modern high-solids paints used in metal protection on bridges and pipelines, give a film (coating) thickness that would require at least two applications of other paint systems.



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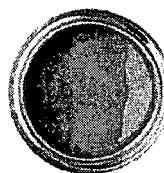
Water-based vs. Solvent-based

What is a Solvent?

Low VOC

Environmental Health and Safety**Regulatory Framework****Eco Labels/Trends**

going green



SHARE

Water-based vs. Solvent-based

Generally, consumers can choose between two types of paints:

- Water-based paints
- Solvent-based paints

As their name indicates, solvent-based paints, sometimes referred to as "oil-based" or "alkyd" paints, contain a significantly higher level of organic solvents than water-based paints. These solvents are responsible for the strong odour noticeable in buildings that have been freshly painted. They are also potentially hazardous for both human health and for the environment which is why concerted efforts are being made to reduce or remove their presence in paints without negatively impacting on paint performance.

Today, water-based paints dominate and account for roughly 80% of paints sold in the residential market.

The function of organic solvents in a paint relates to certain properties it brings – it facilitates the paint's application, it's drying, and the formation of a regular paint film. During application and drying, the solvent evaporates. Ideally a dry paint film no longer contains solvent. However when they evaporate, these solvents release Volatile Organic Compounds (VOCs) into the atmosphere, with a negative, toxic impact on the environment.

Fifty years ago, virtually all paint was solvent-based. Today, advances in paint technology mean that modern, water-based paints, often referred to as acrylic emulsions, are increasingly replacing organic solvents across a broad range of paint applications and surface areas (and account for 80% of architectural paints). Legislation is in place to support this trend.

Spear headed by (but not limited to) regulatory developments in California, we continue to see stricter paint VOC regulations across the US and Canada. In terms of total VOC's, 100 g/l paints are very common today. And predictions are that most manufacturers will have 50 g/l in the near future.

From a performance standpoint, advances in paint technology mean that high quality water-based paints are in many respects equal to or superior to their solvent-based equivalents. High quality acrylic emulsions offer excellent durability, quick drying time, and the emission of less odor.



PQI Tip: A simple way of finding out if a paint is water-based or solvent-based is to check on the label about how to clean brushes. Solvent-based paints need to be cleaned with white spirit or turpentine, water-based paints can be cleaned with warm, soapy water.

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Mercury Compounds

Hazard Summary-Created in April 1992; Revised in January 2000

Mercury exists in three forms: elemental mercury, inorganic mercury compounds (primarily mercuric chloride), and organic mercury compounds (primarily methyl mercury). All forms of mercury are quite toxic, and each form exhibits different health effects.

Acute (short-term) exposure to high levels of elemental mercury in humans results in central nervous system (CNS) effects such as tremors, mood changes, and slowed sensory and motor nerve function. Chronic (long-term) exposure to elemental mercury in humans also affects the CNS, with effects such as erethism (increased excitability), irritability, excessive shyness, and tremors. Human studies are inconclusive regarding elemental mercury and cancer.

Acute exposure to inorganic mercury by the oral route may result in effects such as nausea, vomiting, and severe abdominal pain. The major effect from chronic exposure to inorganic mercury is kidney damage. Animal studies have reported effects such as alterations in testicular tissue, increased resorption rates, and abnormalities of development. Mercuric chloride (an inorganic mercury compound) exposure has been shown to result in forestomach, thyroid, and renal tumors in experimental animals.

Acute exposure of humans to very high levels of methyl mercury results in CNS effects such as blindness, deafness, and impaired level of consciousness. Chronic exposure to methyl mercury in humans also affects the CNS with symptoms such as paresthesia (a sensation of pricking on the skin), blurred vision, malaise, speech difficulties, and constriction of the visual field. Methyl mercury exposure, via the oral route, has led to significant developmental effects. Infants born to women who ingested high levels of methyl mercury exhibited mental retardation, ataxia, constriction of the visual field, blindness, and cerebral palsy.

Please Note: The main sources of information for this fact sheet are EPA's [Integrated Risk Information System \(IRIS\)](#), which contains information on inhalation chronic toxicity and the [RfC](#) for elemental mercury, oral chronic toxicity and the [RfD](#) for inorganic and methyl mercury, EPA's [Mercury Study Report to Congress](#), and the Agency for Toxic Substances and Disease Registry's (ATSDR's) [Toxicological Profile for Mercury](#). Other secondary sources include the World Health Organization's [Environmental Health Criteria Documents on Methyl Mercury and Inorganic Mercury](#).

Uses

Elemental mercury

Uses

Elemental mercury

- Elemental mercury is used in thermometers, barometers, and pressure-sensing devices. It is also used in batteries, lamps, industrial processes, refining, lubrication oils, and dental amalgams. (1)

Inorganic Mercury

- Inorganic mercury was used in the past in laxatives, skin-lightening creams and soaps, and in latex paint. In 1990, EPA canceled registration for all interior paints that contained mercury. Mercury use in exterior paint was discontinued after 1991. Although most agricultural and pharmaceutical uses of inorganic mercury have been discontinued in the United States, mercuric chloride is still used as a disinfectant and pesticide. (1,2)

Methyl mercury

- Methyl mercury has no industrial uses; it is formed in the environment from the methylation of the inorganic mercurial ion. (1)

Sources and Potential Exposure

Elemental Mercury

- A major source of exposure for elemental mercury is through inhalation in occupational settings. (1,3,4)
- Another source of exposure to low levels of elemental mercury in the general population is elemental mercury released in the mouth from dental amalgam fillings. (3,4,5)

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CARBON DISULFIDE PRODUCTION BY REACTION OF ELEMENTAL SULFUR WITH CARBONIZED LIGNITE AND WOOD CHARCOAL

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Carbon disulfide was produced at about the same high rates, using either lignite chars or wood charcoal. A maximum space velocity of 9280 hr.^{-1} was achieved by reaction of sulfur and lignite char at 792°C . Raising the carbonization temperature of chars in nitrogen increased the threshold for reaction with sulfur by as much as 300°C . The activation energy for subsequently reacting chars with sulfur averaged 44,000 cal. per gram mole. Rates were first order with respect to the partial pressure of sulfur, were lowered by increasing the rate of sulfur admission, and were essentially unaffected by char size. High rates of production in a lignite-based process could offer advantages in the manufacture of carbon disulfide, if yields were attractive. Determining optimum yields will be a major objective in a forthcoming pilot plant program.

CARBON DISULFIDE ranked 49th in value among major organic chemicals in 1959, when production of 563,000,000 pounds was valued at \$28,200,000 (7). The production of carbon disulfide is closely tied to the manufacture of regenerated cellulose (rayon and cellophane), which accounts for an estimated 72 to 80% of United States consumption. Other uses are in the manufacture of carbon tetrachloride, rubber accelerators, and insecticides.

The traditional method for the manufacture of carbon disulfide has been to make wood charcoal and sulfur react at approximately 850°C . in externally heated retorts or electric furnaces (3). Production of carbon disulfide from sulfur and methane has rapidly supplanted the charcoal process and was estimated to account for 40% of United States production by 1958 (4). Perhaps 75% of the active capacity now employs the new process (7, 2).

The high price of wood charcoal and the relatively high temperature required for reaction are disadvantages of the charcoal process. This process would be more attractive if a cheaper carbon could be made to react at lower temperatures, but unfortunately substitutes for charcoal have generally proved unsatisfactory because of slow reaction rates. For example, coke requires reaction temperatures hundreds of degrees higher than those used for wood charcoal to produce carbon disulfide at even lower rates.

Carbonized lignite has proved provisionally acceptable as a substitute for charcoal. Laboratory experiments carried out in England have shown that sulfur reacts with chars made from low-rank coal at rates comparable to those with wood charcoal (4). In both East and West Germany, shortage of wood charcoal has forced development to the point where chars made from brown coal are being used commercially (5).

The work done in Europe on the use of low-rank coal for the production of carbon disulfide appears to be of special importance to the lignite-producing areas in the United States.

Sulfur from natural gas has recently become available in the North Dakota lignite area, and the proximity of these raw materials could represent an opportunity for production of carbon disulfide. Potential markets within a reasonable distance could include cellophane plants in Clinton, Iowa, and Tecumseh, Kan.

North Dakota lignite is considered to be a reactive fuel, causing one to expect that it would react readily with sulfur. To substantiate this, a program of research was instituted by the Federal Bureau of Mines to determine rates of reaction between sulfur and carbonized lignite under various conditions suitable for manufacturing carbon disulfide.

Experimental Procedure

Superheated sulfur vapor in nitrogen at 1 atm. was passed through a fixed bed of char. Approximately 80 cc. of lignite char or 218 cc. of wood charcoal (50 grams of either at specified condition) was contained in a 2 1/2-inch i.d. stainless steel reactor which was inserted in a muffle furnace. Liquid sulfur was metered into a vaporizer (by displacement with a controlled flow of mineral oil) and nitrogen was added to obtain the desired partial pressure of sulfur. The sulfur and nitrogen were heated in a preheater to approximately 700°C . before being introduced into the reactor, so that the heat required to dissociate S_8 and S_8 to S_2 would not be absorbed in the reaction zone. After reaction, products were separated from unreacted sulfur by condensing the sulfur at 140°C . and filtering the cooled gases to remove sublimed sulfur dust. Water was removed by calcium chloride, after which the carbon disulfide was separated in a condenser cooled with sublimed carbon dioxide. Gas leaving the condenser contained nitrogen, hydrogen sulfide, and carbonyl sulfide.

Figure 1 is a schematic drawing of the apparatus.

Chars Used in Experiments

Lignite chars were prepared in the laboratory by heating raw lignite in a nitrogen atmosphere to a predetermined temperature and holding at that temperature for 1 to 2 hours. For some runs, the effective maximum carbonization tempera-

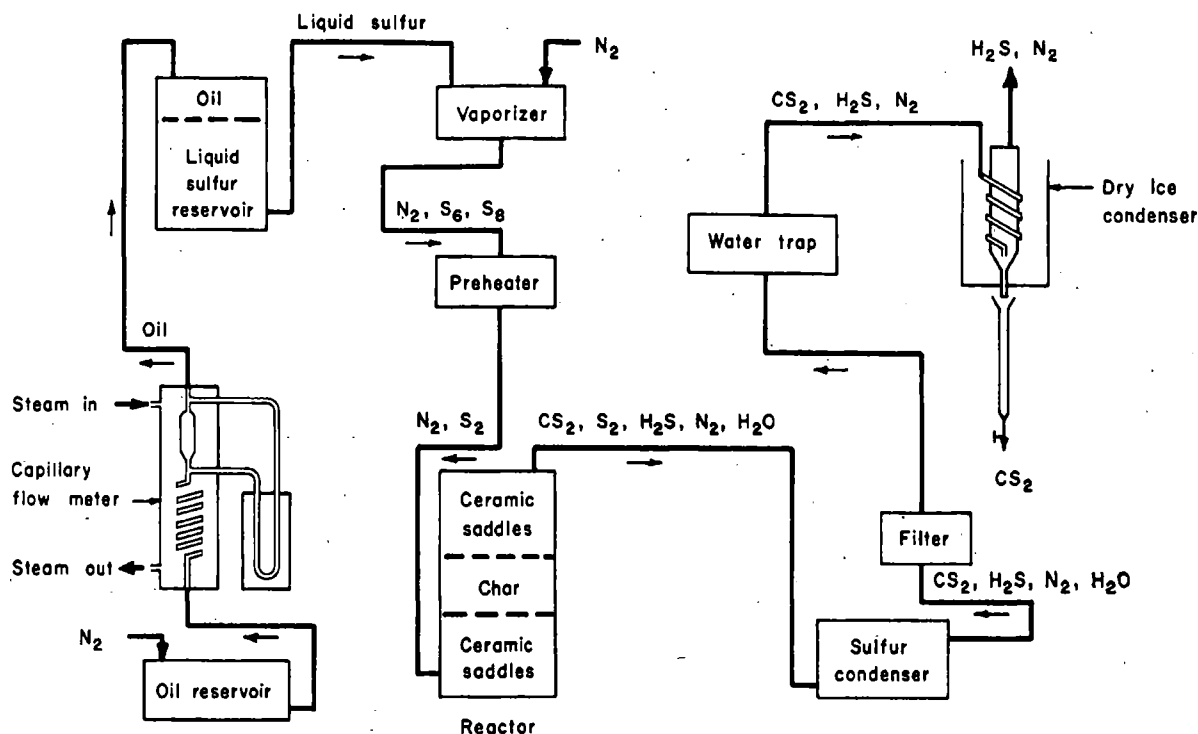


Figure 1. Bench-scale apparatus for production of carbon disulfide

ture was altered by additional heating to higher temperatures in nitrogen before the admission of sulfur during production tests. Typical analyses of lignite chars carbonized at various temperatures are given in Table I. Bulk density of lignite chars tested was 0.6 gram per cc.

The hardwood charcoal used in control experiments was similar to that used for commercial production except for size, which was through 2 on 3 mesh to through 8 on 10 mesh, compared to lumps over 1 1/4 inches for commercial production. The bulk density of the wood charcoal was 0.23 gram per cc. Analyses of wood charcoal are given in Table II.

Product Analysis

Carbon disulfides from wood charcoal and lignite char were similar in appearance and in infrared spectra. Color ranged from pale yellow to essentially colorless. Density at 24° C. was 1.256 grams per ml., compared to 1.257 grams per ml. for pure carbon disulfide. Infrared spectra indicated slight contamination with carbonyl sulfide and an unidentified contaminant absorbing at 9.22 and 14.05 microns.

The majority of the tests were run with ceramic saddles supporting the char and also filling void volume above the char. Carbon disulfide from these tests had only very slight hydrocarbon contamination, indicating that the ceramic packing catalyzed the reaction between sulfur and the volatile matter in the char. Removing the ceramic packing from

above the char greatly increased infrared absorption at the 3.4-micron wavelength characteristic of C-H bonds.

Variables Affecting Production Rate

The rate of a gas-solid reaction is in general controlled by one of two resistances. The physical resistance associated with the diffusion and adsorption that bring together reactants and disperse products is only moderately affected by temperature and is governed by the velocity of the gas stream and the accessibility of the reactive surface. The chemical resistance that is related to the activation energy needed to excite molecules to reaction is greatly affected by temperature, as indicated by the Arrhenius equation which predicts a rate-temperature dependence approximately proportional to $e^{E\Delta T/RT^2}$ where E is the activation energy, T the absolute temperature, and R the gas constant.

Reaction Temperature

Data in Figure 2 for individual experiments on reaction temperature indicate a rapid and continuous rise in production rate with increased temperature. The data presented are for wood charcoal; however, the same continuous effect was noted for lignite char. Reactivity of the char represented by rates corrected to the original amount of fixed carbon present

Table I. Analyses of Carbonized Lignite

Carbonization Temp., ° F.	Proximate Analyses, ^a %				Ultimate Analyses, ^b %					
	Moisture	Volatile matter	Fixed carbon	Ash	Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur	Ash
Raw lignite	32.7	27.7	32.6	6.9	6.5	42.7	0.5	40.6	0.4	9.3
500	3.4	38.0	49.3	9.4	4.5	62.3	1.1	17.8	0.7	13.7
900	3.7	19.5	63.1	13.7	3.0	69.0	1.2	9.8	0.5	16.6
1300	0.8	6.3	80.7	12.2	1.4	76.8	1.1	3.6	0.6	16.6
1700	0.7	2.5	82.0	14.9	0.7	77.2	0.4	1.9	0.7	19.1

^a Proximate analyses are for chars actually used in carbon disulfide production. ^b Ultimate analyses are, except for ash content, typical of chars used.

Table II. Analysis of Wood Charcoal

Proximate Analysis, %		Ultimate Analysis, %	
Moisture	3.23	Hydrogen	3.31
Volatile matter	18.12	Carbon	80.49
Fixed carbon	75.12	Nitrogen	0.38
Ash	3.53	Oxygen	12.20
		Sulfur	0.09
		Ash	3.53

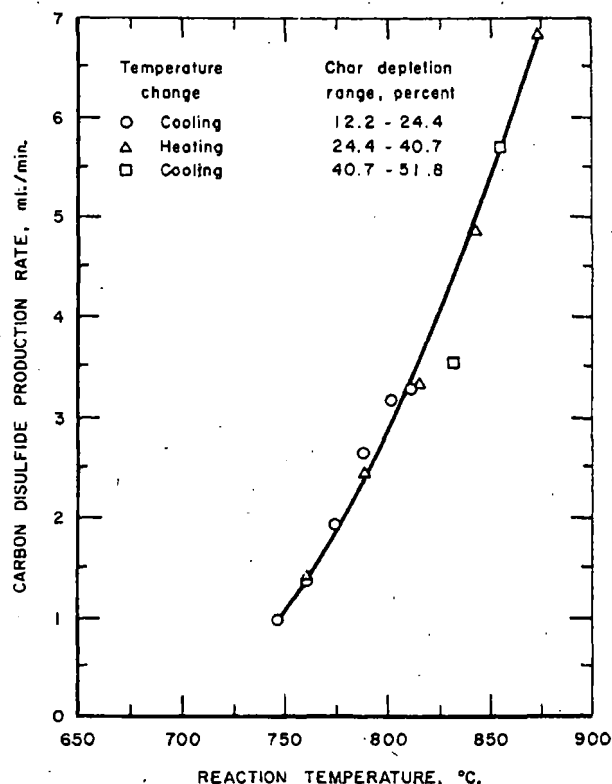


Figure 2. Carbon disulfide production rate vs. reaction temperature for wood charcoal

Rates corrected to initial fixed-carbon content

in the char was essentially constant for char depletions up to 50%.

The simple correlation between rate and reaction temperature presented in Figure 2 did not hold for larger groups of data from several experiments conducted in different temperature ranges. These experiments (Figure 3) were conducted on wood charcoal and lignite char carbonized at 900° F. by raising the temperature of char in nitrogen to the vicinity of the temperature range to be investigated and then introducing sulfur. The temperature was varied after admission of sulfur to determine the effect of reaction temperature in the range being investigated.

The rates thus determined described a series of parallel curves (Figure 3). The placement of these curves fell in the order of the temperatures at which sulfur was first admitted to the reactor, indicating a temperature-related effect that was either activation by sulfur vapor or prior deactivation by nitrogen in the absence of sulfur.

Madon and Strickland-Constable mentioned that chars were deactivated by heating above 500° C. in nitrogen, but gave no details (4). In the present study, the effect was also established

to be deactivation by nitrogen; in the absence of sulfur the maximum temperature in nitrogen governed the reactivity of the char regardless of the lower temperature at which sulfur was later introduced. Since all carbonization of lignite was carried out in nitrogen, the maximum temperature of exposure to nitrogen is designated in this report as the maximum carbonization temperature, regardless of whether this maximum occurred during heating before addition of sulfur or during a separate carbonization.

In view of the observations noted, the data in Figure 3 can be considered to represent separate correlations of production rate vs. reaction temperature at various values of the maximum carbonization temperature. These data for wood charcoal and lignite char were treated statistically as separate groups to determine average activation energies and empirical deactivation functions. Results of the regression calculations are represented by the curves in Figure 3, which are plots of a modified Arrhenius equation. The first term is the customary Arrhenius correlation, whereas the second is an empirical term to account for the offset caused by variation in the maximum carbonization temperature, T_n .

Rate equation for production from 50 grams of wood charcoal:

$$\ln r = \frac{-44,930}{RT_s} + \frac{748}{T_n^{0.508}} + 6.00 \quad (1)$$

Rate equation for production from 50 grams of lignite char:

$$\ln r = \frac{-43,950}{RT_s} + \frac{1228}{T_n^{0.589}} + 6.83 \quad (2)$$

where r = production rate expressed as space velocity of gaseous carbon disulfide at 800° C. and 1 atm. hr.⁻¹

R = gas constant, 1987 cal./gram mole - ° K.

T_n = maximum carbonization temperature in nitrogen, ° K.

T_s = sulfur reaction temperature, ° K.

From Equations 1 and 2, the average activation energies for wood charcoal and lignite char were 44,930 and 43,950 cal. per gram mole, respectively. These values indicate a high degree of temperature dependence, representing a doubling in rate for every 30° C. temperature rise at 700° C. There was, however, a considerable variation in the degree of temperature dependence between experiments; the standard deviations from the average activation energies were 11,124 and 15,610 cal. per gram mole. This deviation accounts in part for the displacement of the curves from the data in Figure 3.

The values of activation energy determined in current experiments were higher than those previously reported by Madon and Strickland-Constable, which were 12,000 and 14,000 cal. per gram mole, respectively, for wood charcoal and coal char (4). The difference between 45,000 and 12,000 cal. per gram mole, as well as the large standard deviations observed for the current data, strongly suggests an extraneous factor acting independently of reaction temperature. Although no very definite pattern can be observed from the data, there is an indication that the apparent activation energy is increased by elevating the threshold reaction temperature and is decreased by raising the rate of sulfur admission.

Carbonization

Using lignite for manufacturing carbon disulfide may or may not require precarbonization to reduce the quantity of volatile matter entering the process with the raw material. A decision to require precarbonization would depend on yields of by-

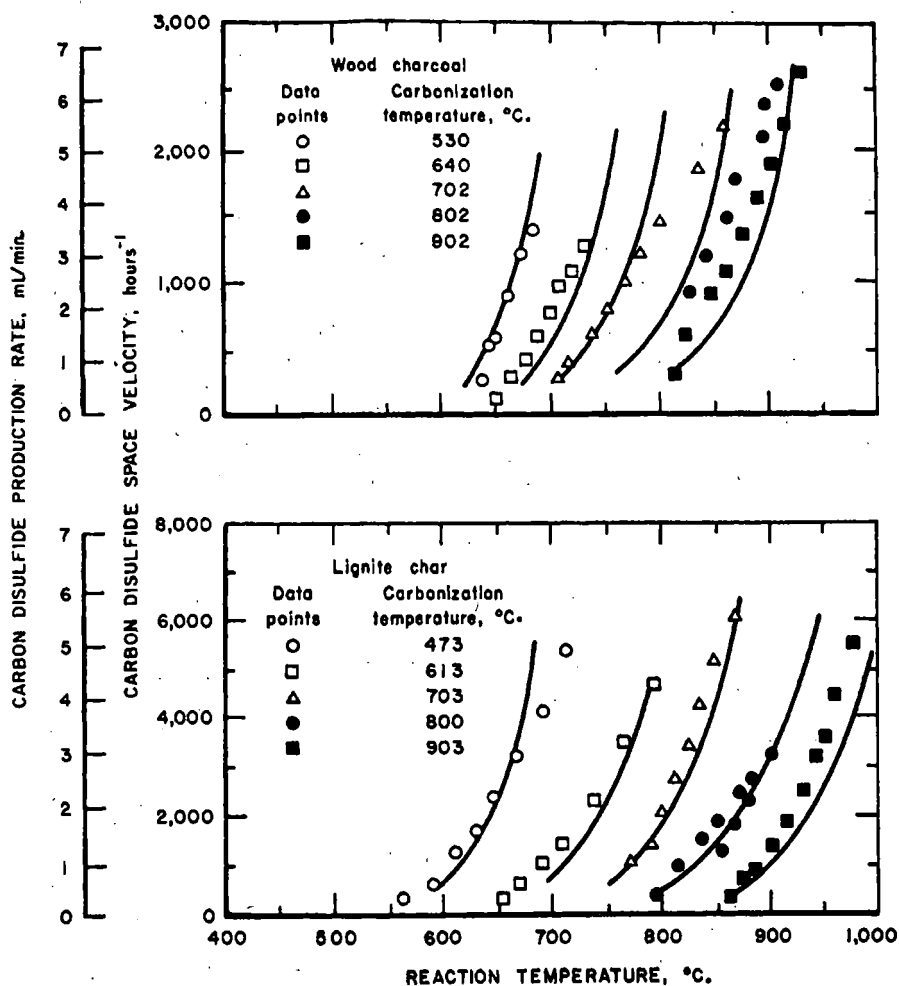


Figure 3. Correlation of carbon disulfide production rates vs. reaction temperature from Equations 1 and 2

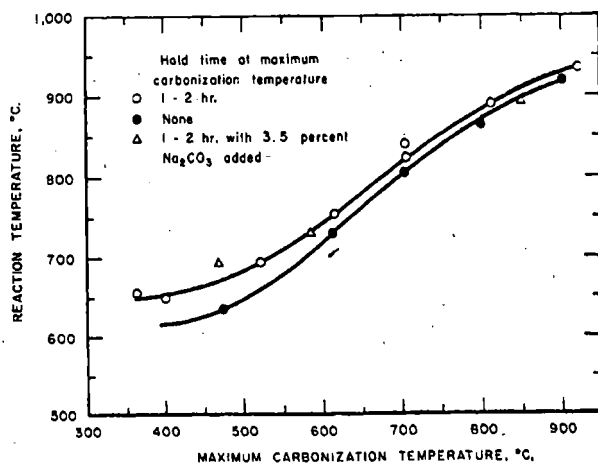


Figure 4. Variation in reactivity of lignite chars with increasing carbonization temperature

Based on comparison of reaction temperatures required to produce carbon disulfide at 2 ml/min.

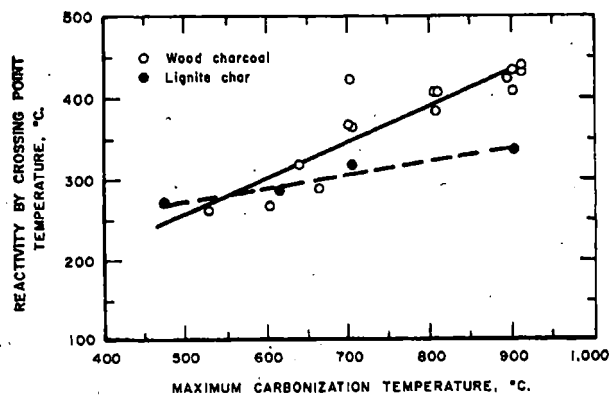


Figure 5. Reactivity of char residue after carbon disulfide production

products and the difficulties encountered in their separation. These factors were not investigated. Further experiments were conducted, however, to determine the effects of carbonization procedure on production rates.

In experiments already described, the maximum carbonization temperature was experienced during the heating period before reaction, and the hold time at the maximum temperature was very brief. A separate series of experiments was run on lignite chars which were carbonized in nitrogen and held at the maximum temperature from 1 to 2 hours. Data for these experiments are compared in Figure 4 with data for lignite chars without appreciable hold time. Both curves represent combinations of reaction temperature and maximum carbonization temperature that resulted in a constant production rate of 2 ml. per minute. The lower the reaction temperature indicated by the correlation, the greater are the reactivity of the char and the ease of reaction.

The correlations presented in Figure 4 illustrate the deactivation that occurs with increasing carbonization temperature. The displacement between the two curves indicates that an extended hold time of up to 2 hours does slightly increase the amount of deactivation, but it is a relatively small effect compared with the controlling influence of the maximum carbonization temperature.

The curves in Figure 4 indicate that the progress of deactivation with increased temperature is less pronounced at high and low temperature extremes than it is in the median temperature interval from 600° to 700° C. Of particular interest is the carbonization temperature below which no significant deactivation occurs. While operating difficulties prevented studies below a carbonization temperature of 360° C., the nearly equivalent results at 360° and 400° C. show there is no apparent deactivation in this temperature range. Deactivation cannot be considered important below 500° C., and deactivation based on industrial reaction temperatures is not excessive at carbonization temperatures to 700° C.

It has been reported that the reaction of sulfur with chars from German brown coal was catalyzed by the addition of alkali carbonates (5). During carbonization of lignite in this study, the addition of approximately 3.5% Na_2CO_3 was observed to have no important effect on the subsequent reaction rates with sulfur. The results of three carbon disulfide production runs using carbonate-treated char are also plotted in Figure 4.

The deactivation occurring with carbonization in nitrogen is also confirmed by a correlation that exists between the carbonization temperature and the crossing-point temperature of the char residue after partial reaction with sulfur. The crossing-point temperature is a measure of the temperature at which the action of a controlled flow of air on a carbonaceous material becomes exothermic. The correlations, which are presented in Figure 5, are significant at 99.9 and 98% confidence levels for lignite char and wood charcoal, respectively.

Particle Size of Char

Particle sizes studied ranged from 0.5 to 0.0164 inch. The gross external area (excluding pore area) was estimated to range from 3.0 to 60.9 square feet per pound based on an empirical equation proposed by Needham (6). Production rates from samples in four size intervals within this range were randomly distributed (at 0.7 probability) over a narrow range from 1.00 to 1.09 ml. per minute. The lack of dependence between production rates and particle size shows that the pore area rather than the gross particle area controls the rate of reaction and that the pore area is equally accessible regardless of particle size over the size range investigated.

Partial Pressure of Sulfur

The effect of partial pressure was measured at three sets of conditions covering the range of production rates from 0.2 to 4.0 ml. per minute. All tests were run on lignite chars at 1-atm. total pressure and at a gas flow rate (sulfur plus nitrogen) of 0.25 gram mole per minute. Data presented in Figure 6 indicate that the rate of production was essentially proportional to the first power of the mean partial pressure, designating the reaction to be of first order with respect to S_2 . Statistically determined slopes for the log-log plots were 0.98, 0.90, and 1.09, respectively, for the three test conditions. The slope determined by pooling data from all three test conditions was 0.984. The individual slopes were not significantly different from a value of 1.0 within 80% confidence limits.

Rate of Sulfur Admission

Experiments on the rate of sulfur admission were carried out at a nominal sulfur partial pressure of 0.5 atm. Results presented in Figure 7 indicate that the rate of production was decreased by increasing the velocity of gas passing through the char bed. Since the velocity of the gas stream through the reaction zone primarily affects the diffusional resistance of the boundary layer surrounding individual char particles, the increased velocity and accompanying turbulence apparently cause an increase in diffusional resistance. This unusual effect

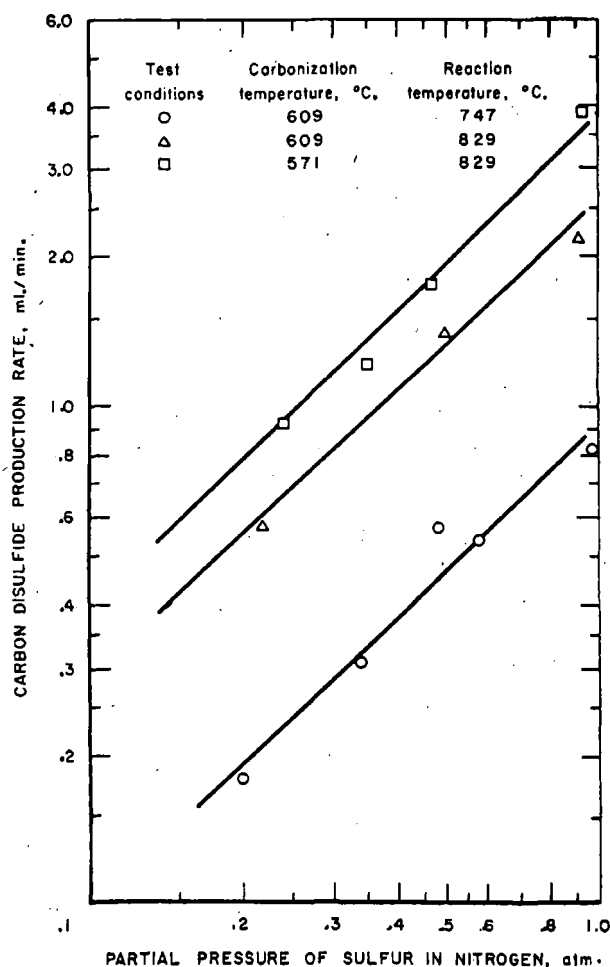


Figure 6. Effect of sulfur partial pressures on carbon disulfide production rates from lignite char

Total pressure 1 atm.

was also noted by Madon and Strickland-Constable (4). Its validity is well established in the present study, the results for which were found to have a linear correlation coefficient of 0.971, indicating significance at the 99.9% confidence level.

Comparison of Carbon Disulfide Production Rates from Lignite Char and Wood Charcoal

Results in the investigation of reaction temperature presented in Figure 3 indicate that the maximum product space velocities were appreciably higher for production from lignite char than from wood charcoal (approximately 6000 hr.⁻¹ for lignite char as compared with 2700 hr.⁻¹ for wood charcoal). Space velocities were calculated as the volume of product at 800° C. and 1 atm. produced per hour per unit volume of reactor.

Because experiments were conducted on equal weights of the two carbon raw materials, the effective reactor volumes differ for the two cases. Without the correction to equal bed volume which is inherent in the calculation of space velocities, the

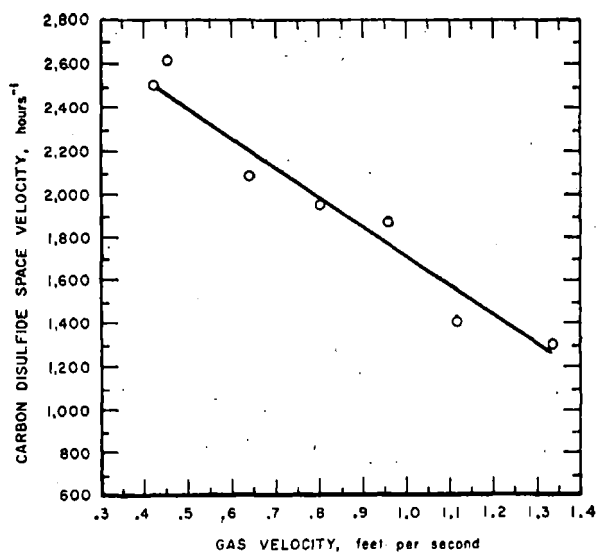


Figure 7 Effect of gas velocity on production rate

Partial pressure of sulfur maintained constant at 0.5 atm. Total pressure 1 atm.

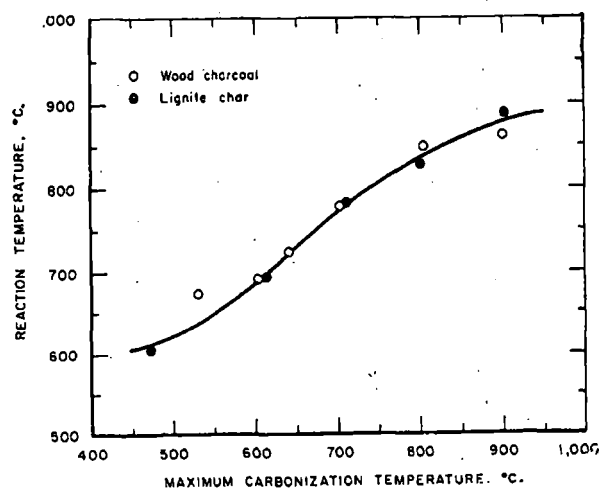


Figure 8. Comparison of reactivities for lignite char and wood charcoal with increasing carbonization temperature

Based on reaction temperature required for carbon disulfide space velocity of 1000 hr.⁻¹

actual rates from 50 grams of lignite char and wood charcoal are nearly the same.

In choosing a good basis for comparing the two carbon sources, consideration should be given to design variables that are of interest in commercial application. Two important variables are reactor volume and temperature. On this basis, a correlation for comparing raw materials should indicate the temperature conditions that are required to achieve the same production per unit volume of char—i.e., space velocity. Such a comparison can be made by referring to Figure 8, which presents the combinations of carbonization and reaction temperatures that will result in a space velocity of 1000 hr.⁻¹ for production from the two chars. The data indicate no important difference between the two chars when compared on the basis of equivalent volume and temperature.

Comparison of Laboratory and Industrial Production Rates

The highest rate of production in the present study was achieved using lignite carbonized at 364° C. and reacting with sulfur at temperatures up to 792° C. At the highest reaction temperature, carbon disulfide was produced essentially at the rate corresponding to equilibrium conversion, which for a sulfur admission rate of 10 grams per minute is 8.5 ml. per minute, or a space velocity of 9280 hr.⁻¹. This and the other space velocities obtained are considerably higher than those reported in previous laboratory investigations, highs for which range from 592 hr.⁻¹ for Madon and Strickland-Constable's experiments (4) to 2700 hr.⁻¹ for Munderloh's work using carbonate-treated chars (5).

The maximum space velocities achieved in the various reported laboratory investigations are all much higher than the value calculated from data for an industrial reactor. The reported production of 3000 pounds per day for an externally heated reactor 10 feet high by 3 feet in diameter (3) represents a space velocity of 32.9 hr.⁻¹ at 800° C. and 1 atm. This value is only about 1/300 of the maximum value experienced in the present study.

Because of limitations in the minimum rate that could be detected in the laboratory apparatus, the 300-fold difference between product space velocities observed in laboratory and commercial practice could not be duplicated in the present study. As a result, the difference cannot be directly explained by the data collected. However, the study does point out factors that could account for continuous differences outside the capability of the laboratory apparatus. One is the deactivation of chars occurring with increasing temperature in a nitrogen atmosphere. A second is the condition of the sulfur admitted to the char bed. In the laboratory, the sulfur was preheated to 700° C. to dissociate S₈ and S₈ to S₂ before admission to the reactor. If in a commercial reactor the sulfur is admitted to the char as a liquid or a gas below the minimum threshold reaction temperature (approximately 600° C.), large quantities of heat must be supplied by the char to heat the sulfur through the temperature range of dissociation to S₂ before reaction can occur, and as a result, a large part of the reactor would be ineffective.

Conclusions

The bench-scale investigation established that sulfur will react with relatively inexpensive lignite chars at moderate temperatures and at rates which are orders of magnitude higher than those which are characteristic of the older charcoal processes. This suggests the possibility of a spectacular modernization in the solid carbon route to carbon disulfide using an inexpensive carbon source.

Based on the favorable results in rate studies, a preliminary cost estimate was performed to determine whether or not further development of a lignite process was warranted. The hypothetical process used for economic evaluation involved the reaction of sulfur with dried lignite at 750° C., assuming by-product yields that represented a 10% loss in sulfur and no credit for potential recovery. Results indicated that the process on this basis would be competitive with current market prices at a plant capacity above 20,000,000 pounds per year.

The favorable indications provided by the rate studies and the cost estimate are not by themselves sufficient to establish the suitability of lignite as a raw material or the complete feasibility of a lignite-based process. Information is lacking on the yields of carbon disulfide from sulfur that can be achieved using various lignite chars, a factor which is highly important to the economics of the process. In addition it is necessary to demonstrate the technical feasibility of continuously admitting

sulfur and char to a compact reaction system to capitalize on the high rates that have been demonstrated.

The solutions to these problems are major objectives in a pilot plant program which has recently been initiated.

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EFFECT OF ORGANOSULFUR COMPOUNDS ON THE RATE OF THERMAL DECOMPOSITION OF SELECTED SATURATED HYDROCARBONS

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The effect of addition of 0.001 to 10 weight % of an organosulfur compound upon the thermal decomposition rate of each of several saturated pure hydrocarbons was studied by batch experiments at 800° F. and elevated pressure. The effects of benzenethiol or *tert*-butyl disulfide upon *n*-hexadecane, 5-*n*-propylnonane, and decahydronaphthalene were studied in detail. Decomposition rates of the branched-chain paraffins were accelerated; those of the saturated hydrocarbons were inhibited. The sulfur compounds less stable than the hydrocarbons all acted in the same direction. Some proposed mechanisms are discussed.

HYDROCARBON fuels used in high speed flight vehicles may become heated to several hundred degrees Fahrenheit before combustion by aerodynamic heating of the fuel tank, by absorption of heat to cool lubricating oil or portions of the engine, or by all three. As a result, gums, sediments, or deposits may be formed in the fuel and cause excessive pressure drop through nozzles and strainers or even complete plugging.

The reactions and conditions leading to the formation of these undesirable products are but poorly understood. The effects stem in part from precursors formed by air oxidation on storage, a reaction which may be catalyzed by trace metal contaminants or by container materials. Some air oxidation may also occur in flight vehicle tanks during aerodynamic heating. The susceptibility to gum and deposit formation also varies with the kinds of hydrocarbons present in the fuel and is increased by the presence of various contaminants containing sulfur or nitrogen. The fact that deposit formation is also a function of previous time-temperature history of the fuel and of various interactions among oxygen, contaminants, catalysts, and inhibitors leads to highly complex phenomena

and sometimes seeming contradictions between the results of different investigators. Most studies have been made with actual fuels, with or without various deliberately added model contaminants.

To help clarify the situation, it is desirable to know the rate of decomposition of selected pure hydrocarbons in the absence of oxygen and how these rates are affected by the presence of specific sulfur compounds which typify the kinds of compounds that may be found in hydrocarbon fuels. Beyond this, hydrocarbons are used in a variety of technical applications which require a fluid thermally stable at high temperatures, and it is important to know the effects of contaminants on decomposition rate.

Sulfur compounds are a universal contaminant in hydrocarbon fuels and are generally present in substantially higher concentrations than nitrogen contaminants. Johnson, Fink, and Nixon (5) and Thompson *et al.* (14, 15) report studies of the amounts of gum and sludge formed upon heating fuels containing small amounts of various sulfur compounds under conditions in which oxygen has access to the fuel. The results

§ 15.1. Transfer of custody and management of orphan corporate and business records.

(a) The Department of State is authorized, under 15 Pa.C.S. § 140, to provide for the transfer on a progressive and phased basis to the custody and management of the Department any or all orphan corporate and business records. These records are corporate and limited partnership filings and recordings which were formally effected in the office of the Clerk of Court of Common Pleas or the office for the recording of deeds or an equivalent row office in a home rule charter county and which are no longer effected in such offices by reason of the enactment of corporate statutes.

(b) Under 15 Pa.C.S. § 140(b), the Department is required to publish in the *Pennsylvania Code* a notice where, as between a county and the Department, custody of all orphan corporate and business records resides. Under this requirement, notice is hereby given that as of September 1, 1996, all orphan corporate records maintained in the 67 counties of the Commonwealth of Pennsylvania have been transferred to the Department of State's Corporation Bureau. The records are available on 16mm microfilm and are accessible to the public.

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A - General - Type General refers to a legal entity with no special attributes such as non profit or religious.

B - Bank - Bank refers to the entity actually existing as a Bank and conducting banking business.

C - Closed Corp - (a) A close corporation is a corporation organized under subchapter 342 whose certificate of incorporation contains the provisions required by Section 102 of this title and, in addition, provides that:

(1) All of the corporation's issued stock of all classes, exclusive of treasury shares, shall be represented by certificates and shall be held of record by not more than a specified number of persons, not exceeding 30; and

(2) All of the issued stock of all classes shall be subject to 1 or more of the restrictions on transfer permitted by Section 202 of this title; and

(3) The corporation shall make no offering of any of its stock of any class which would constitute a "public offering" within the meaning of the United States Securities Act of 1933 [15 U.S.C. Section 77a et seq.] as it may be amended from time to time.

(b) The certificate of incorporation of a close corporation may set forth the qualifications of stockholders, either by specifying classes of persons who shall be entitled to be holders of record of stock of any class, or by specifying classes of persons who shall not be entitled to be holders of stock of any class or both.

(c) For purposes of determining the number of holders of record of the stock of a close corporation, stock which is held in joint or common tenancy or by the entireties shall be treated as held by 1 stockholder.

D - DISC Corp - Domestic International Sales Corporation A domestic corporation meeting certain conditions pursuant to federal Internal Revenue Service codes. For more information please visit www.irs.gov and search DISC.

F - Professional Association - (1) The term "professional service" shall mean any type of personal service to the public which requires as a condition precedent to the rendering of the service the obtaining of a license or other legal authorization, and which, by reason of law, prior to June 7, 1969, could not be performed by a corporation. In addition, and by way of example without limiting the generality thereof, the personal services which come within this chapter are the personal services rendered by architects, certified or other public accountants, chiropractors, chiropractors, doctors of dentistry, doctors of medicine, optometrists, osteopaths, professional engineers, veterinarians, and, subject to the Rules of the Supreme Court, attorneys-at-law.

(2) The term "professional corporation" means a corporation which is organized, under this chapter, for the sole and specific purpose of rendering professional service, and which has as its shareholders only individuals who themselves are duly licensed or otherwise legally authorized within this State to render the same professional service as the corporation.

G - General Partnership - Partnership" means an association of two or more persons formed under Section 15-202 of this title, predecessor law or comparable law of another jurisdiction to carry on any business, purpose or activity.

I - Regulated Investment Corp. - A domestic corporation that elects to be treated as an RIC as defined by Section 851 of the federal Internal Revenue Code for tax purposes. For more information please visit www.irs.gov and search RIC.

L - LLP or LLLP - A partnership (whether General or Limited) that has filed a statement of qualification pursuant to 6 DEL.C. § 15-1001.

N - Non Title 8 - This refers to an entity that is not regarded as a general corporation pursuant to Title 8.

R - Non-profit or Religious - This description type refers to a corporation that sets forth in its certificate of incorporation or subsequent documents that it is a non-profit corporation. The "Religious" literal does not infer that, in every case, the corporation is for Religious purposes only. The intent is to define the corporation as Non-Profit, charitable corporation which maybe formed for Religious purposes.

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Partnership (whether General or Limited Liability Partnership)
Unincorporated Non-Profit Association

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- C - Cancelled** - A certificate of Cancellation has been voluntarily filed by the entity to terminate its existence. This certificate is filed when an entity has dissolved and at the completion of winding up the entity.
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- O - AR filed, Tax delinquent** - This represents a corporation that has filed the required annual report, however there are still delinquent taxes due.
- P - Revoked** - A Limited Liability Partnership (LLP) that has not filed their Annual Report. The Statement of Qualification or Statement of Foreign Qualification of the LLP has been revoked by the Secretary of State.
- Q - AR delinquent, Tax paid** - This represents a corporation that has paid taxes in full, however the required annual report has not been filed.
- R - Forfeited-Resigned** - A Limited Partnership, Limited Liability Company or Partnership that has on record a Certificate of Resignation of registered agent and the appointment of a new registered agent was not filed within the designated period of 30 days.
- S - Surrendered** - A Certificate of Voluntary Dissolution before issuance of shares or before beginning of business has been filed with the Division of Corporations.
- T - Transfer** - A Certificate of Transfer has been filed and the result of such transfer is the cessation of its existence as an entity of the State of Delaware.
- U - AR delinquent, Tax due** - This represents a corporation that has not filed the required annual report and there are delinquent taxes due.
- V - Void** - A corporation that failed to pay its annual franchise tax for a period of 1 year or a Foreign Corporation that has not filed their annual reports within a 2 year period.
- W - Withdrawal** - A voluntary Certificate of Withdrawal has been filed by the Corporation which is registered/qualified to do business in Delaware as a Foreign Corporation but domestic in another jurisdiction, to terminate its authority to transact business in the State of Delaware.

X - Ceased Good Standing - This represents an entity that failed to pay their annual taxes timely. For example: 2002 taxes due June 1, 2003 were not received by end of day June 1, 2003.

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Every corporation is required by law to file an annual report which is due March 1 annually. This field reflects the most current tax year that has a report on file.

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Foreign means that this entity is domiciled in another jurisdiction but registered/qualified to do business in Delaware.

FILING HISTORY EFFECTIVE DATE

Delaware law provides for a future effective date of a document and this field indicates the effective date of the document as set forth in the contents of said document.

FILE NUMBER

A unique identifier assigned to each entity incorporated, formed, qualified or registered with the Division of Corporations.

FILING HISTORY FILING TIME

The time of day the document was received for filing.

TOTAL AUTHORIZED SHARES

Any stock corporation may authorize shares of stock that may be issued at a future date. This field represents the current total number of shares authorized by the company's certificate of incorporation or subsequent amending documents.

ENTITY NAME

The current name of an entity as set forth in their certificate of incorporation or formation; or as amended by

subsequent documents.
